Electron Transport in Plasma-Produced, Disordered Nanocrystal Films

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Funding:
NSF MRSEC DMR-1420013
DOE Center for Advanced Solar Photophysics
AOR MURI Grant W911NF-12-1-0407

Overview

- Introduction
- Plasma synthesis of nanocrystals
- Electronic transport in NC films (P-doped Si)
- Another try: ZnO NC films
- Semitransparent Luminescent Solar Concentrators
- Conclusions

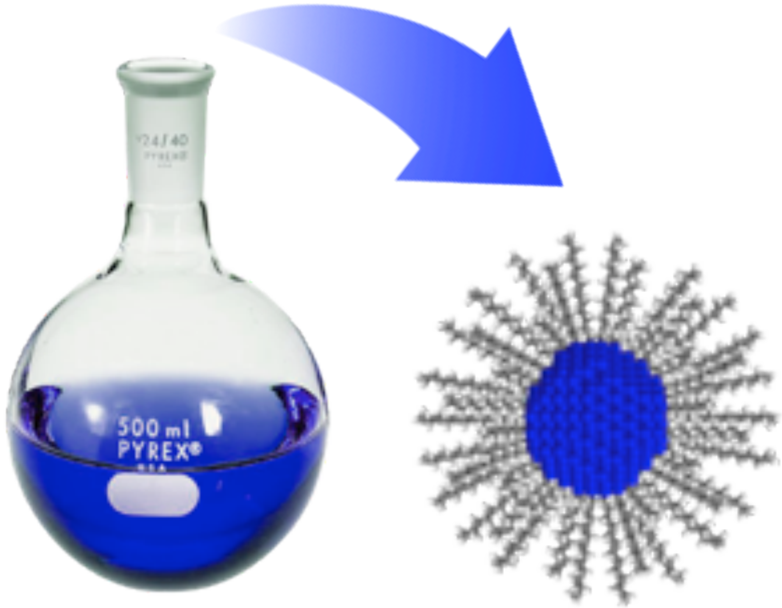
On the market products

Samsung Quantum dot TV

DuPont-Innovalight Si ink

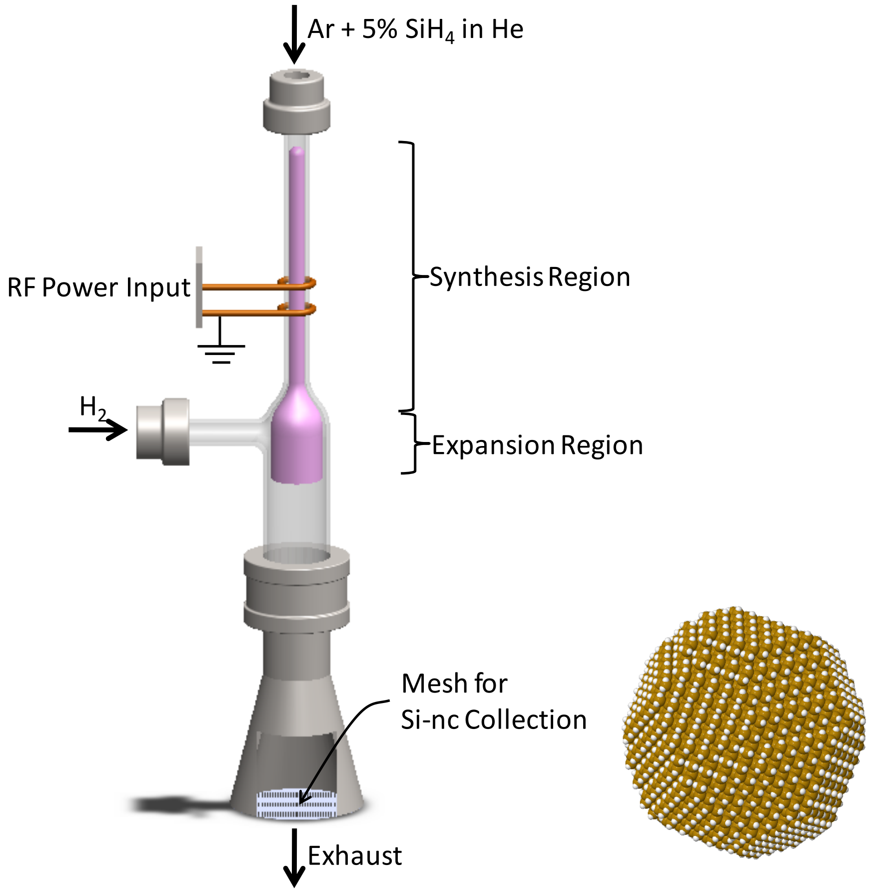
Quantum dot syntheses

Liquid Phase Synthesis



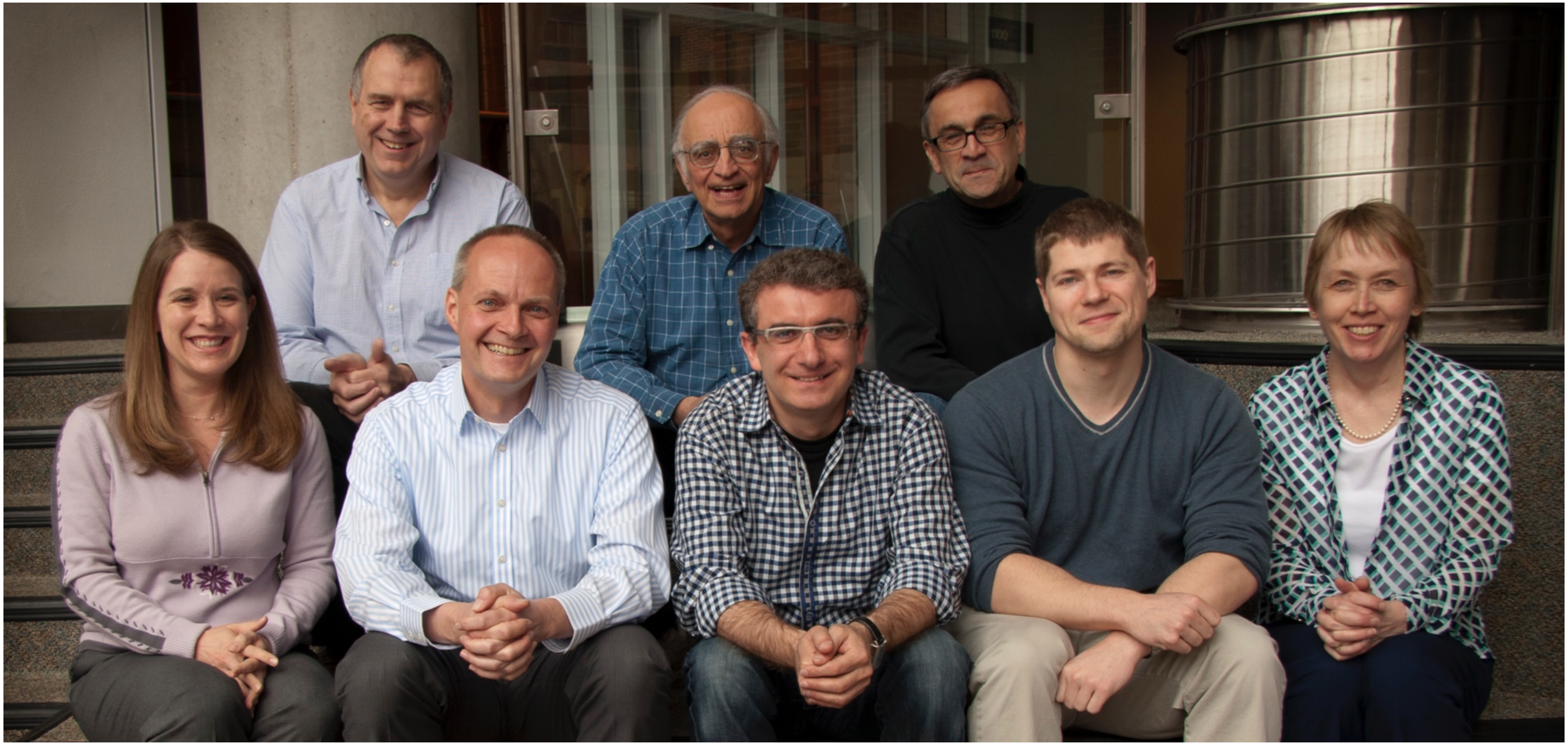
ionically bound NCs (PbX, CdX; X=S, Se, Te)

Gas Phase Synthesis



covalently bound NCs (Si, Ge, nitrides,…)

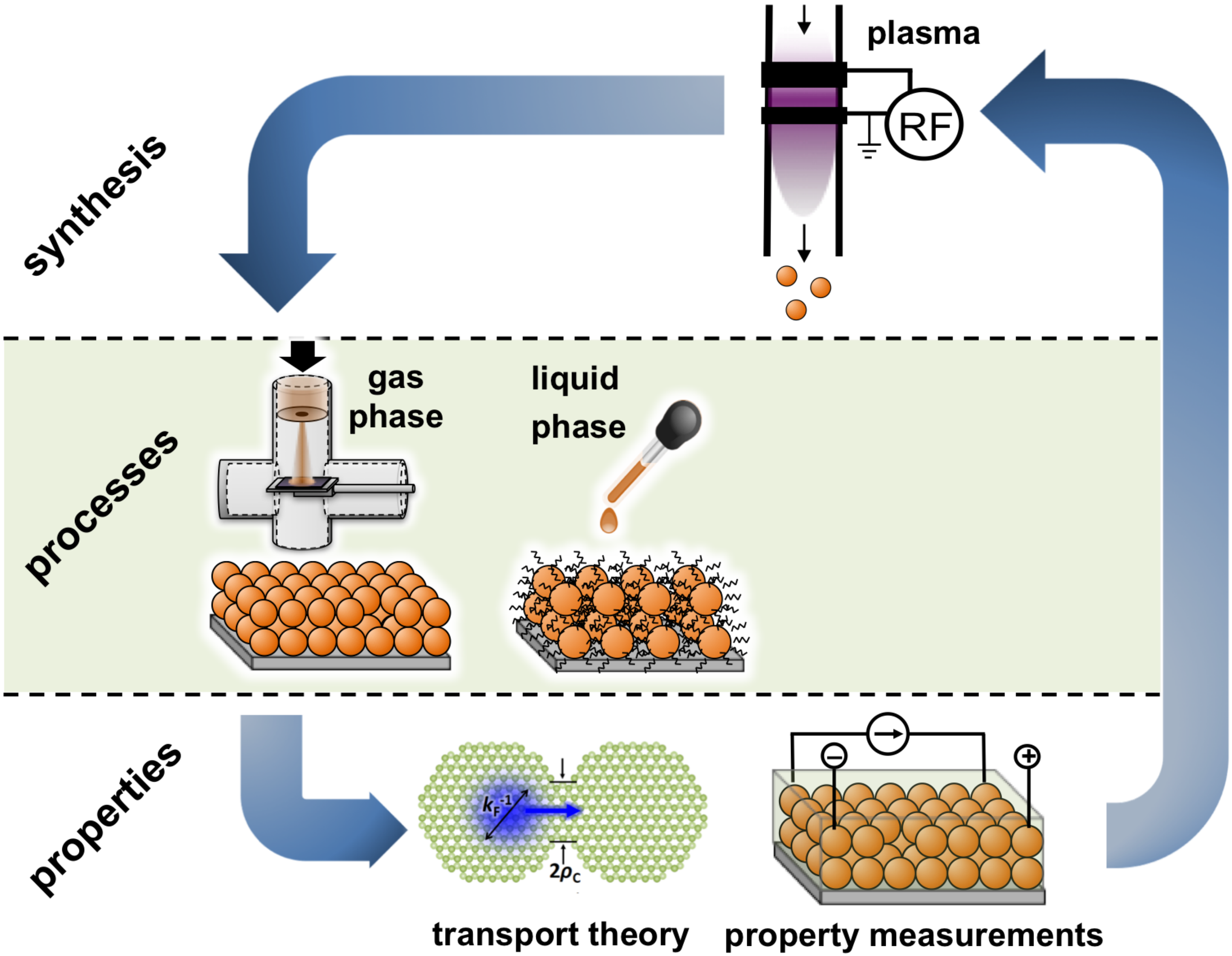
MRSEC IRG-2: Sustainable Nanocrystal Materials



Stephen Campbell, Boris Shklovskii, Eray Aydil

Christy Haynes, Uwe Kortshagen, Andre Mkhoyan, Chris Hogan, Lorraine Francis

IRG activities

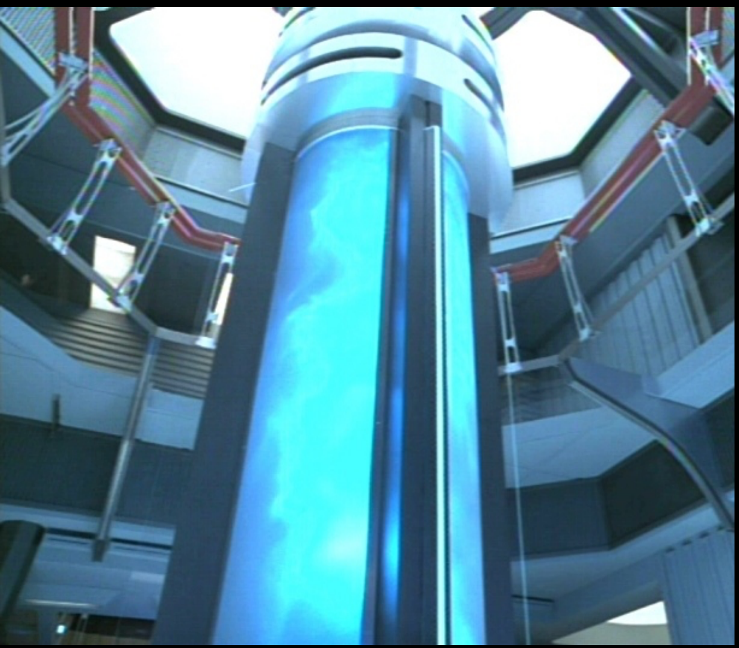


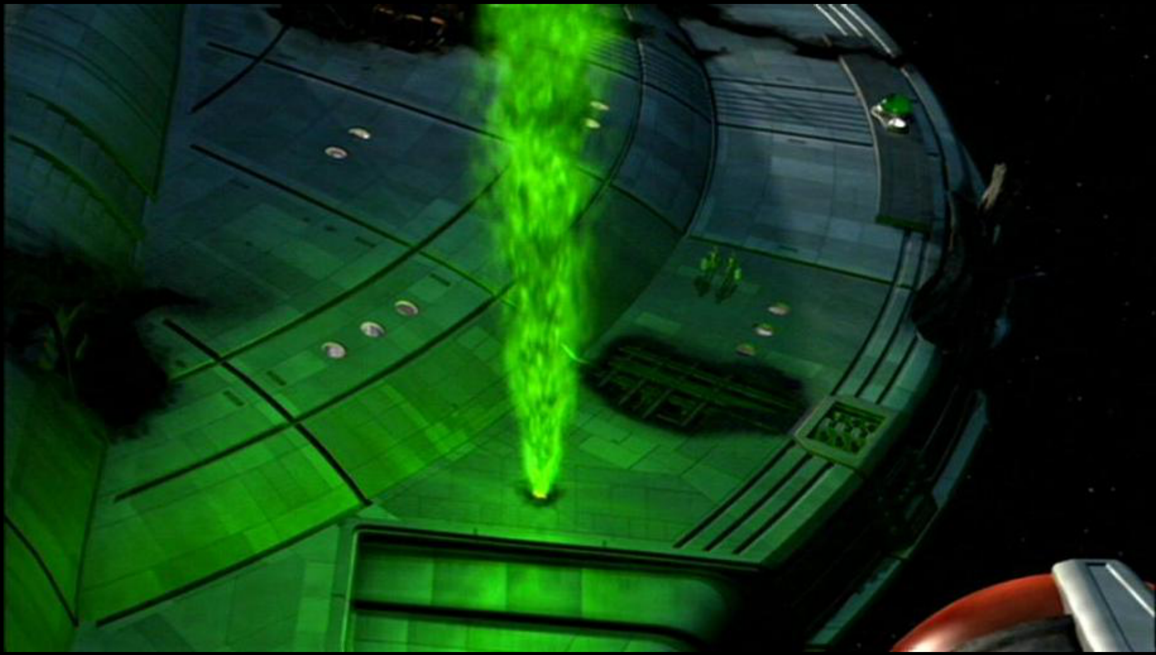
L. Mangolini

E. Thimsen

Plasma synthesis of nanocrystals

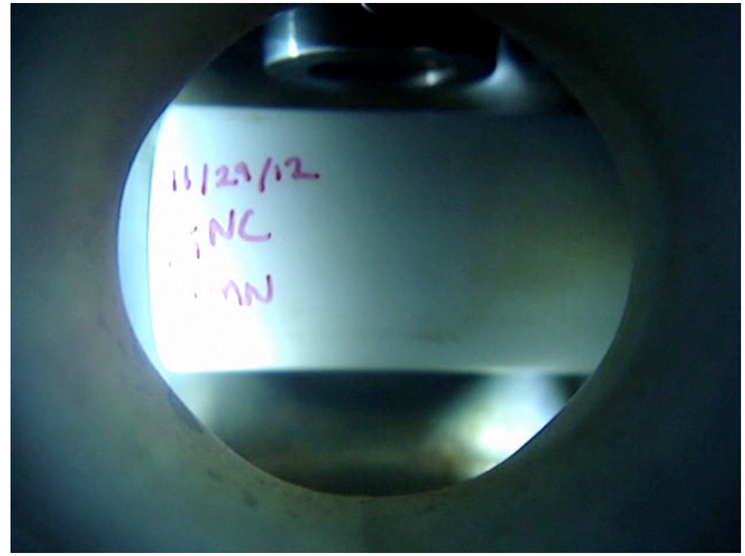
Plasmas: The medium of the future!





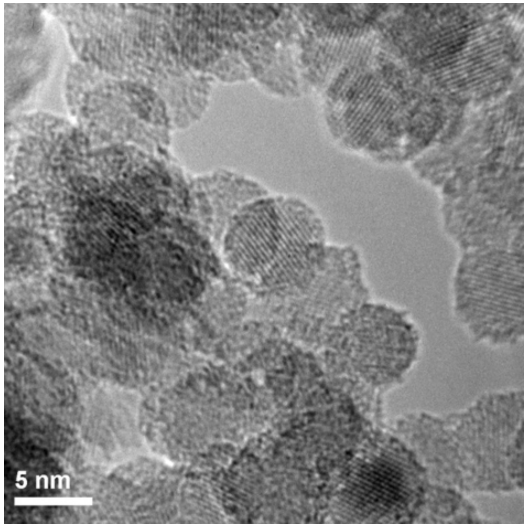
Plasmas synthesis of group IV nanocrystals

L. Mangolini, E. Thimsen and U. Kortshagen,
Nano Letters **5(4)**, 655 (2005)

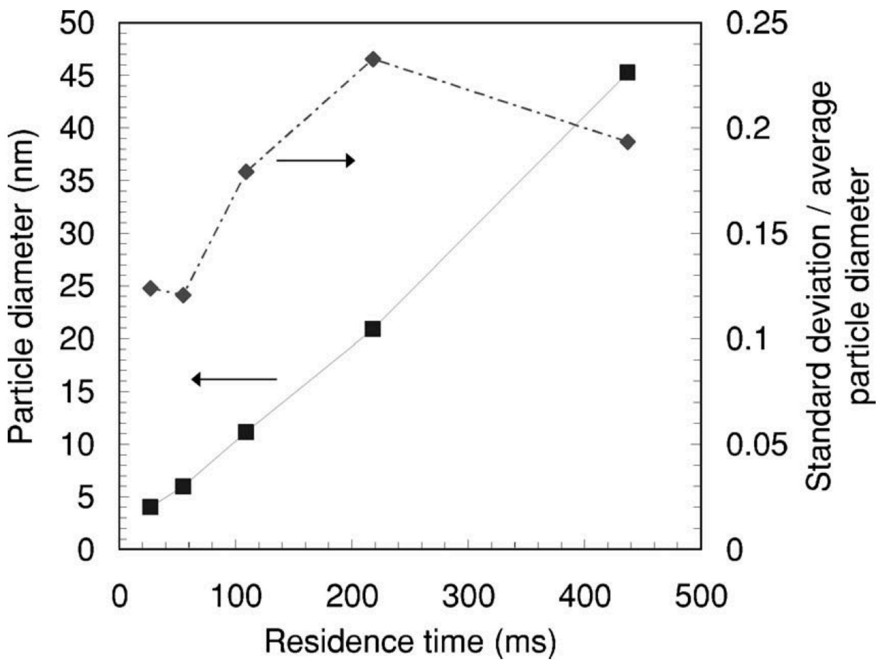


• gas pressure:	few 100 Pa
• gas temperature:	~300-500 K
• electron temp.:	~30,000-50,000 K (3-5 eV)
• ionization fract.:	$\sim 10^{-5}$

Plasmas synthesis of group IV nanocrystals



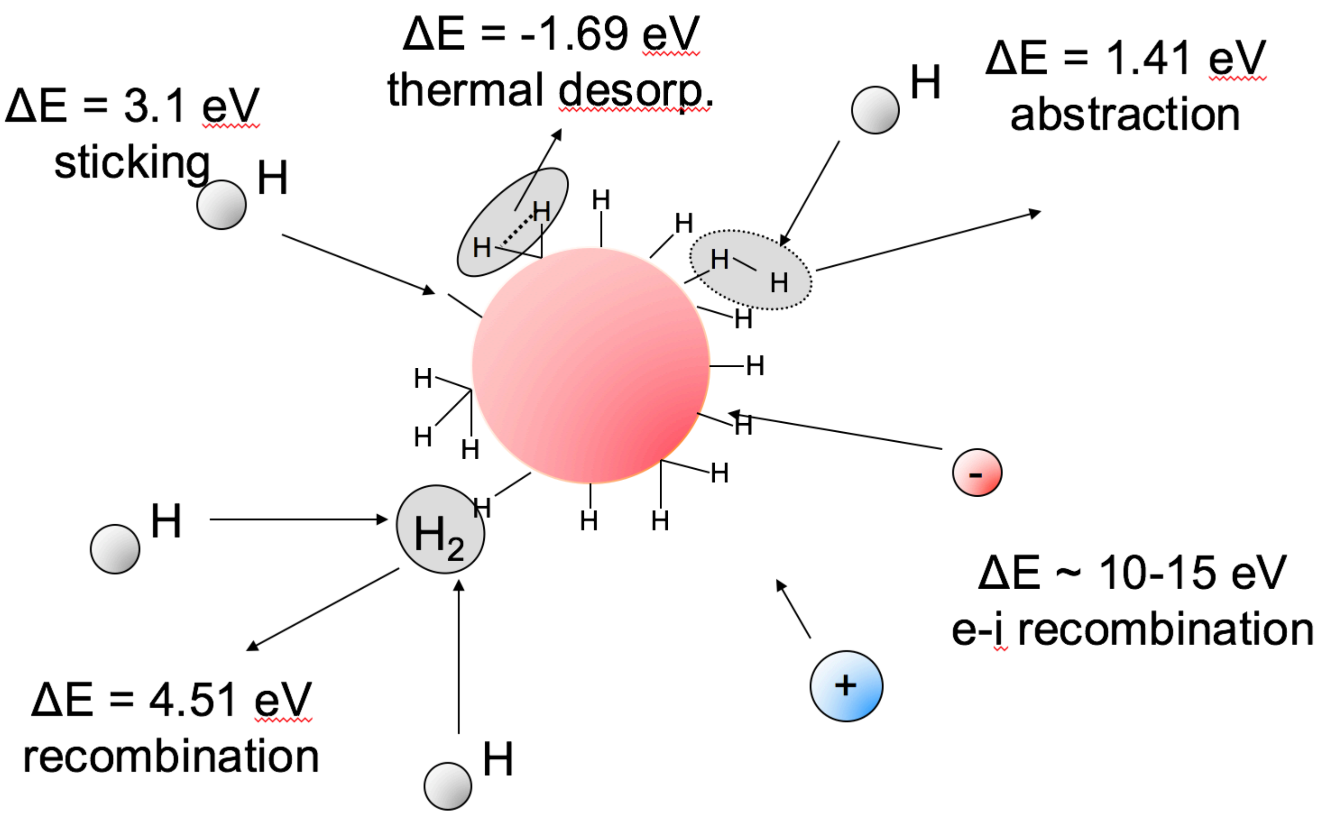
L. Mangolini et al., Nano Letters (2005)



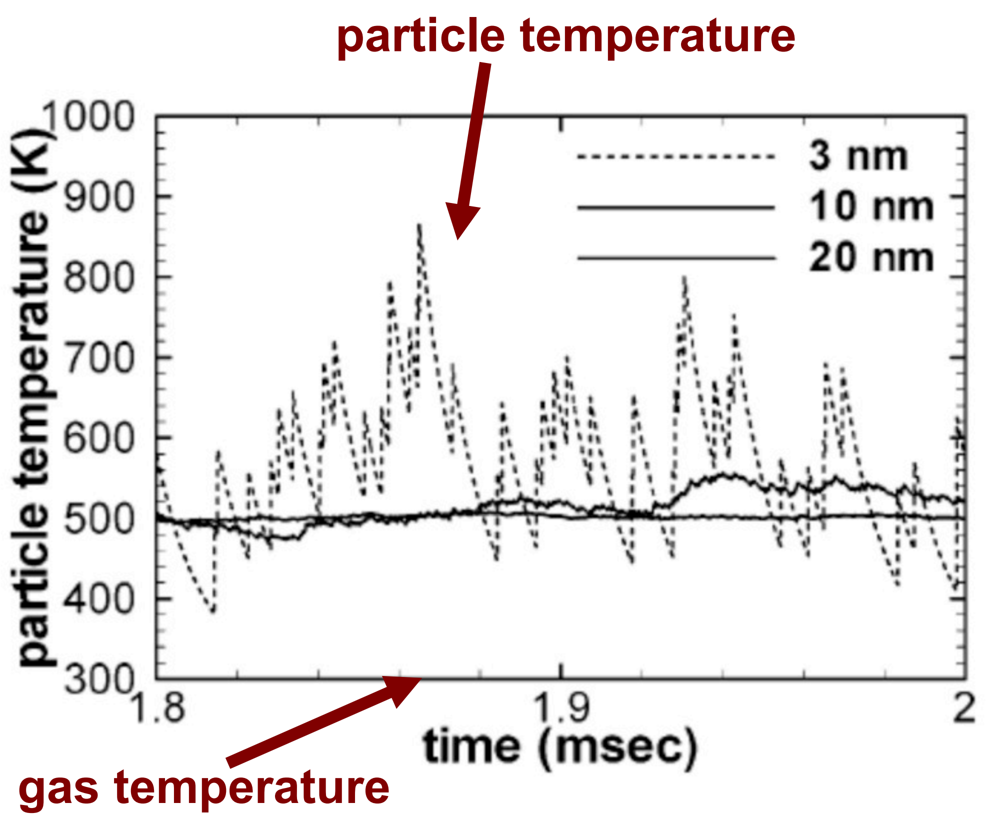
R. Gresback, Z. Holman, U. Kortshagen, Appl. Phys. Lett. **91**, 093119 (2007) (for Ge NCs from $GeCl_4$)

- materials that require high temperature
- particle size control through residence time
- relatively good monodispersity

Heating of NCs in plasmas



Heating of NCs in plasmas

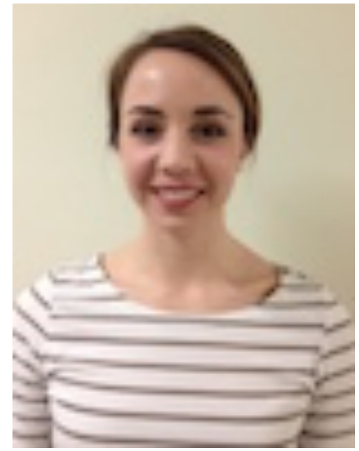


L. Mangolini et al., Nano Letters (2005)

David Rowe

Katelyn Schramke

Nic Kramer



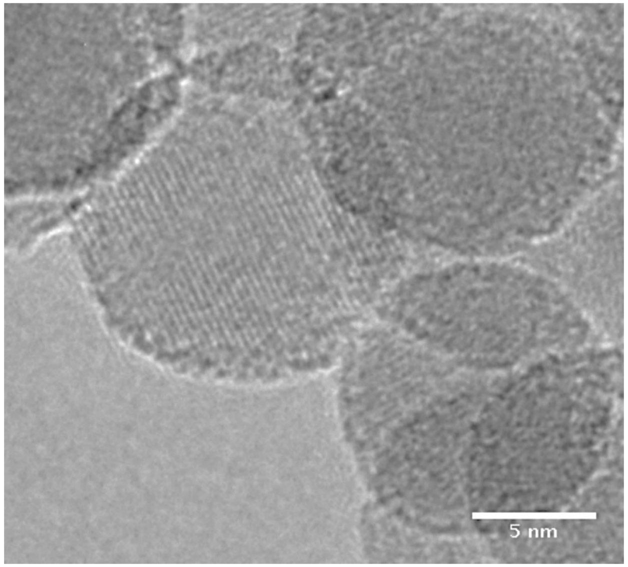
Katharine Hunter

Nick Bedford
(NIST, Boulder)

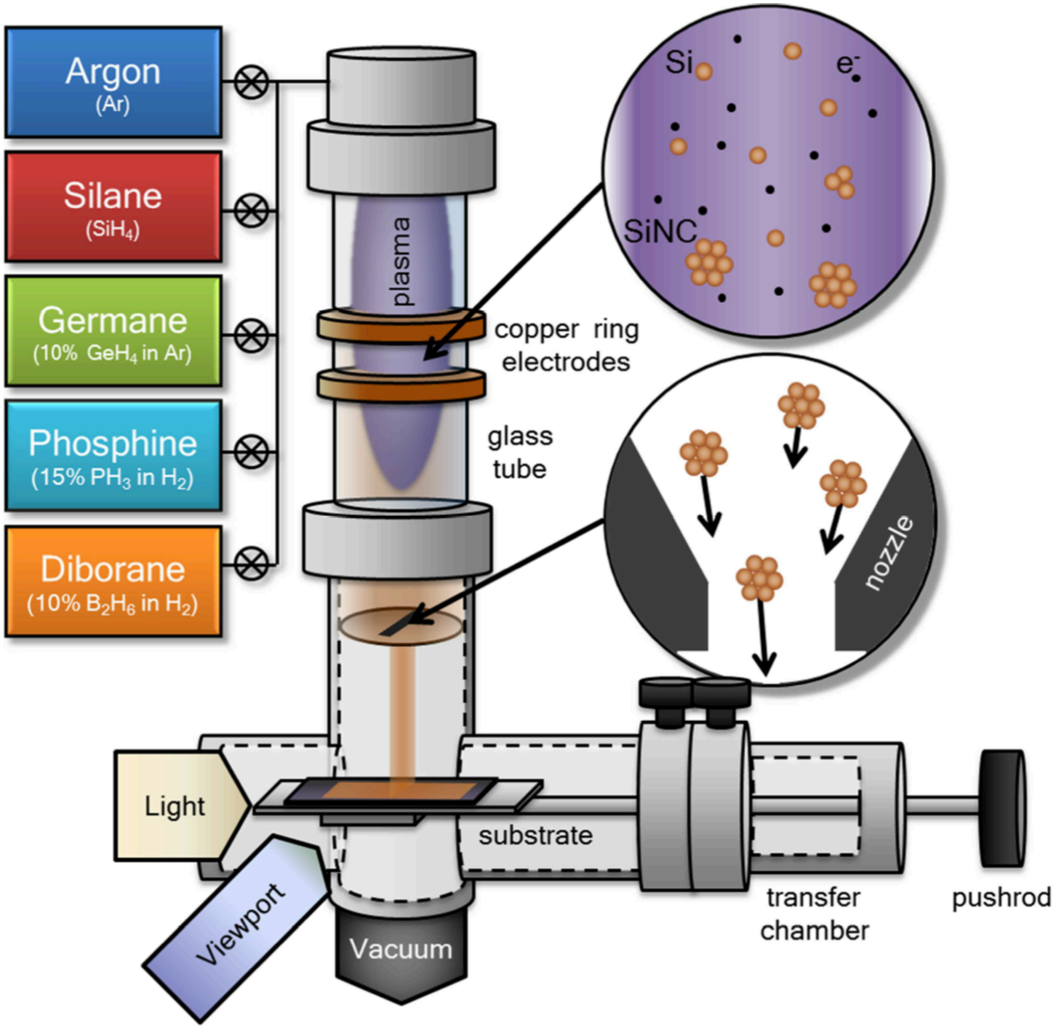
Nanocrystal doping and plasmonics

Not this kind of plasma doping!

Doping Si nanocrystals

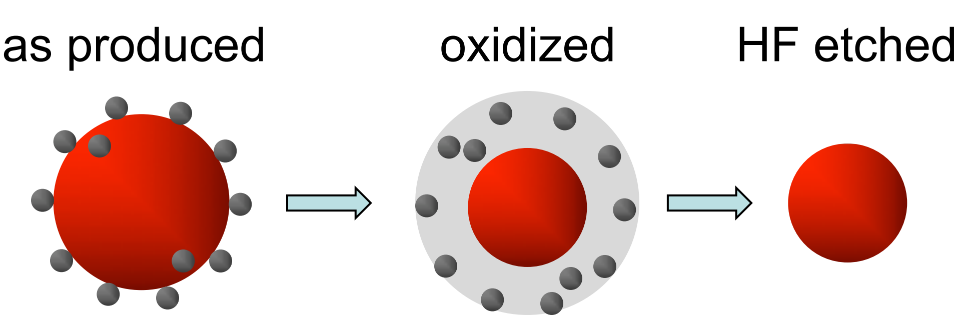


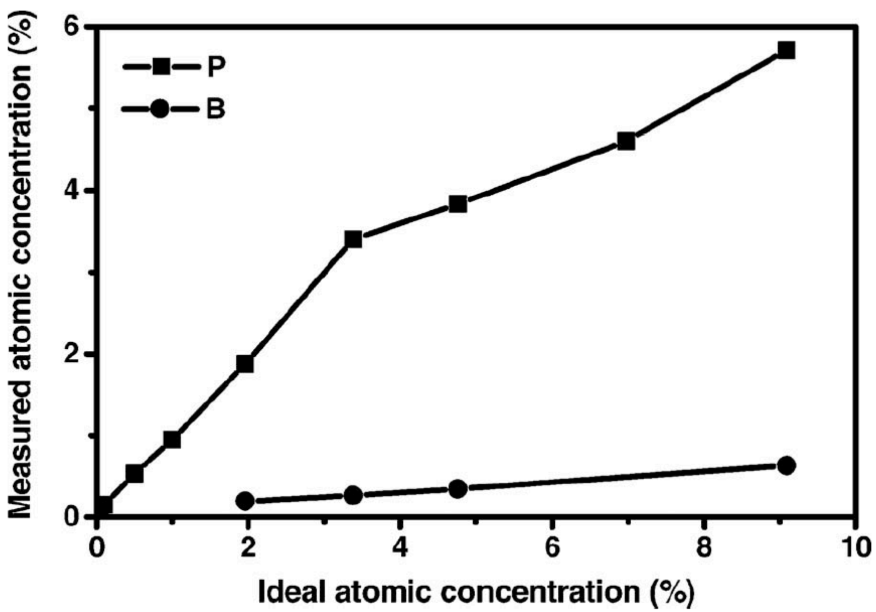
Nanoparticle size: ~ 8 nm

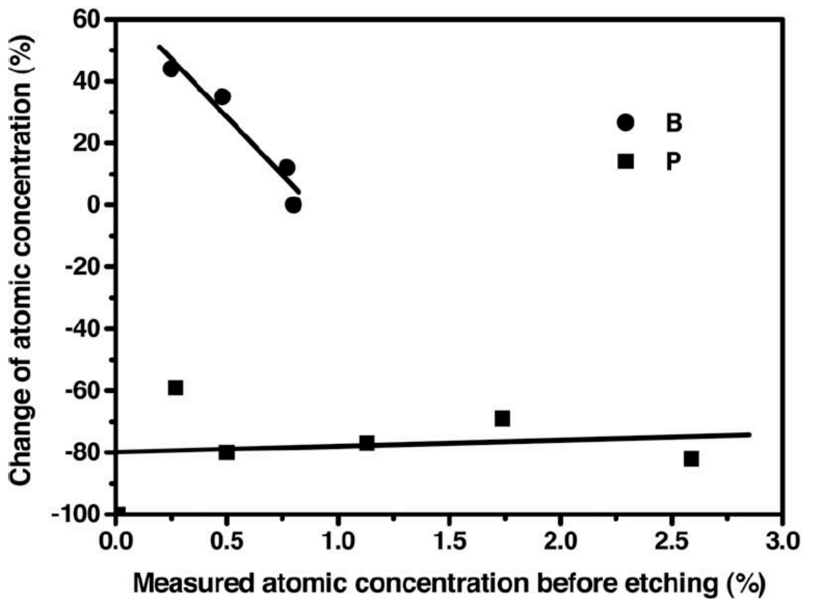


D. Rowe, Ph.D. thersis, UMN

First attempts at plasma doping

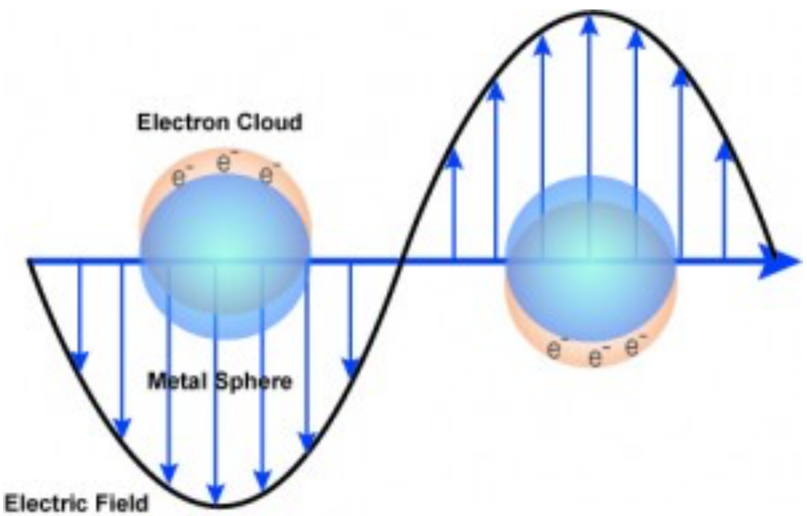




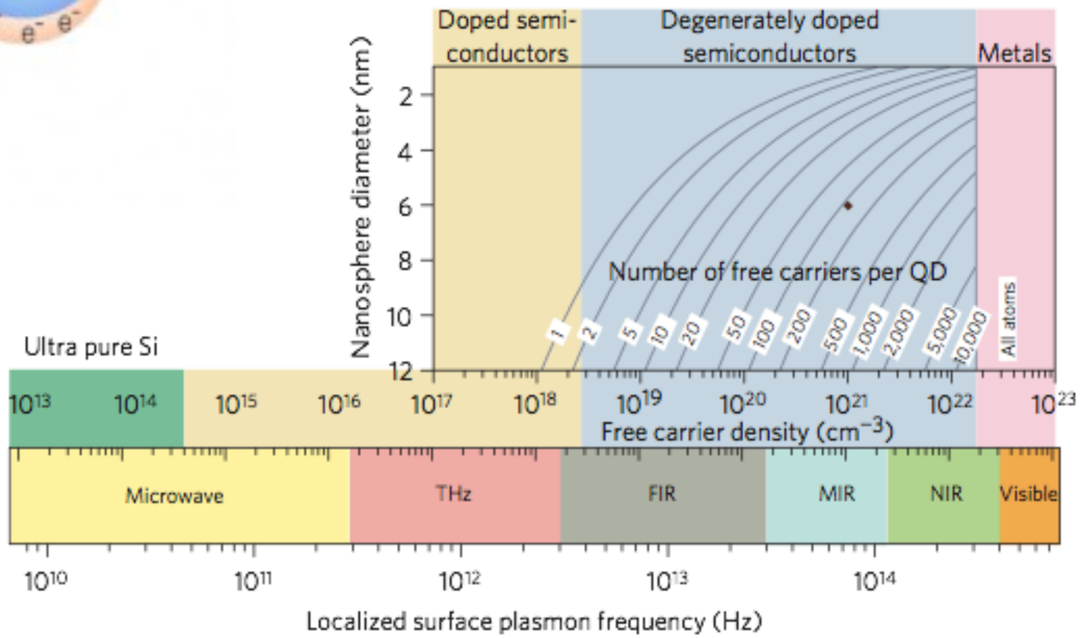


X. D. Pi and R. Gresback, R. W. Liptak ,S. A. Campbell, U. Kortshagen, Appl. Phys. Lett. **92**, 123102 (2008).

Doped nanocrystals as IR absorbers

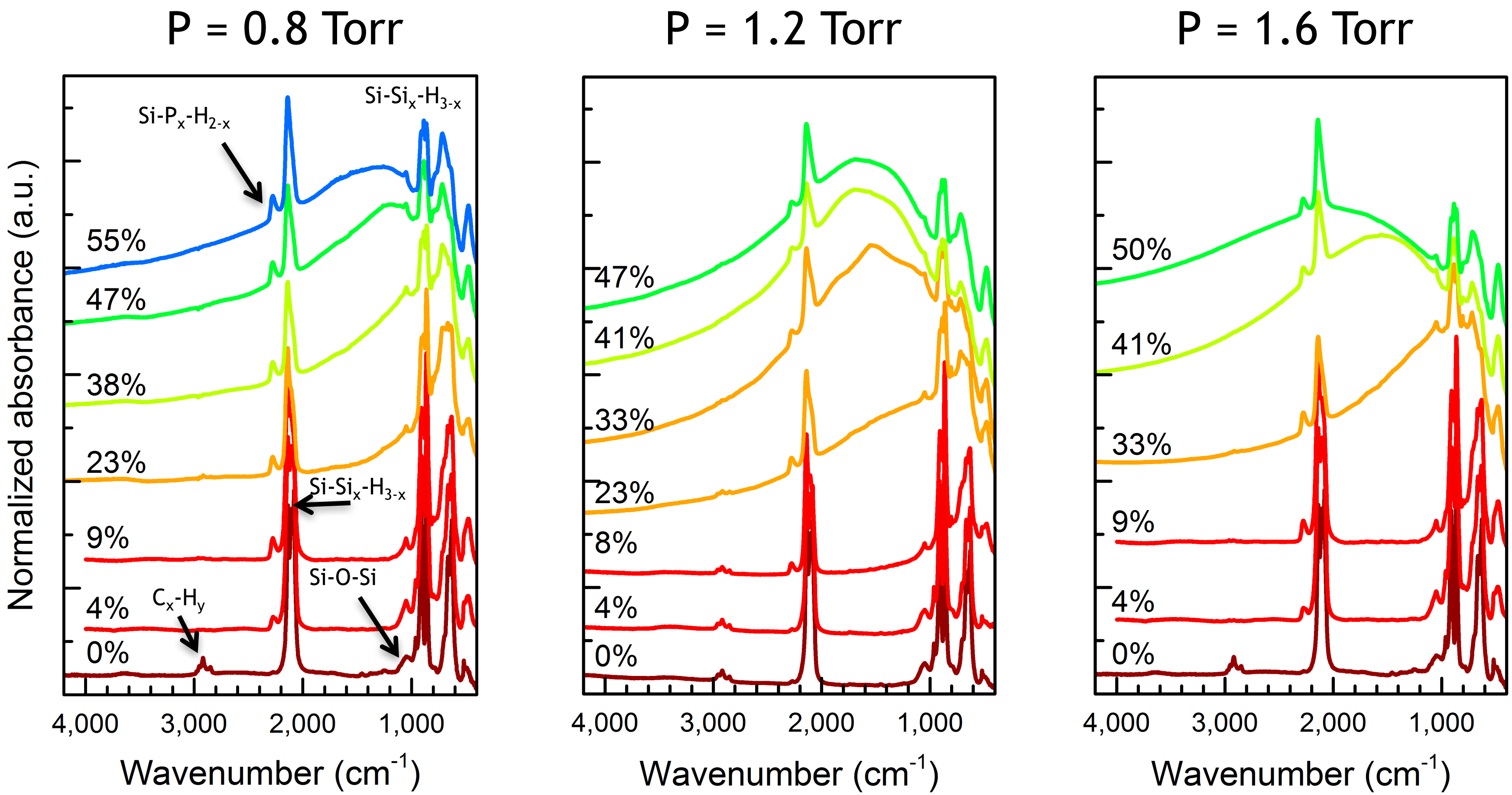


www.nanocomposix.com



J.M. Luther, P.K. Jain, T. Ewers, and P. Alivisatos, Nature Materials 10, 361-6 (2011).

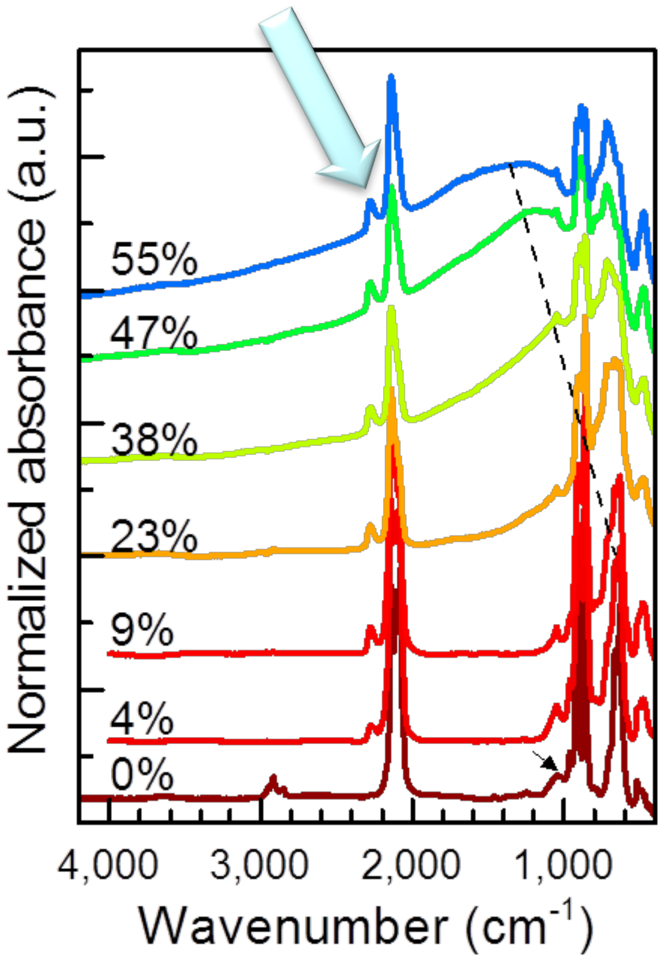
Si NC LSPR in IR

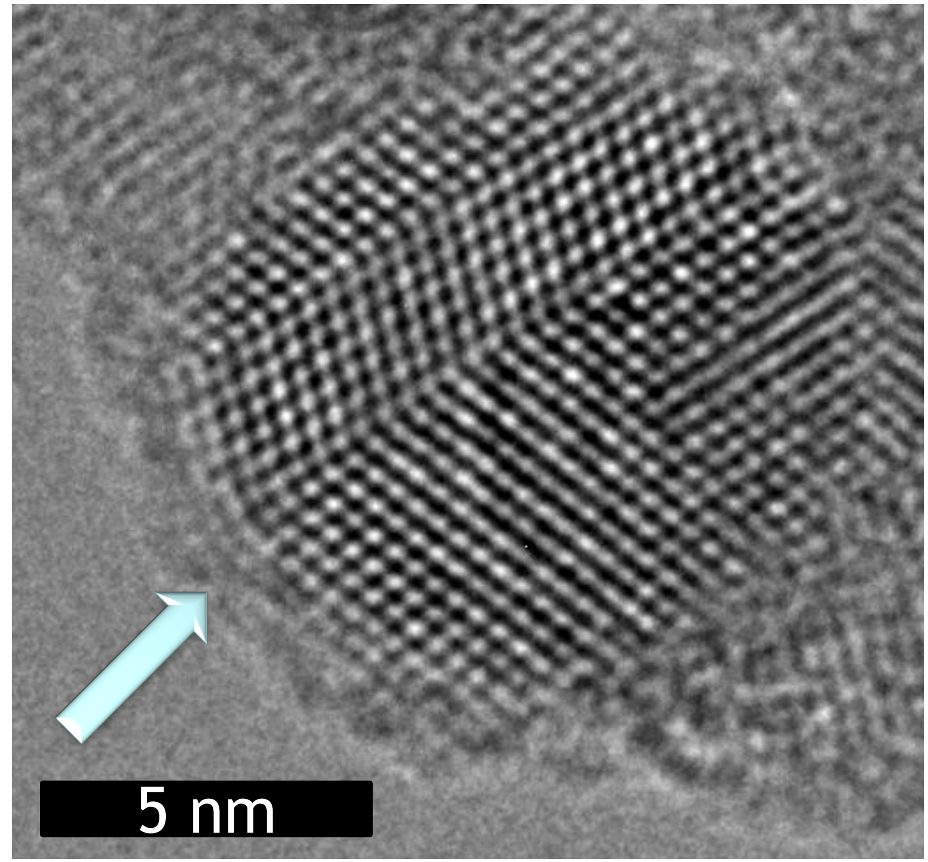


$$X_{PH3} = [PH_3]/([PH_3]+[SiH_4])\text{x}100\%$$

D. J. Rowe, J. S. Jeong, K. A. Mkhoyan, and U. R. Kortshagen, Nano Letters **13**, 1317 (2013)

Hypothesized location of dopant…

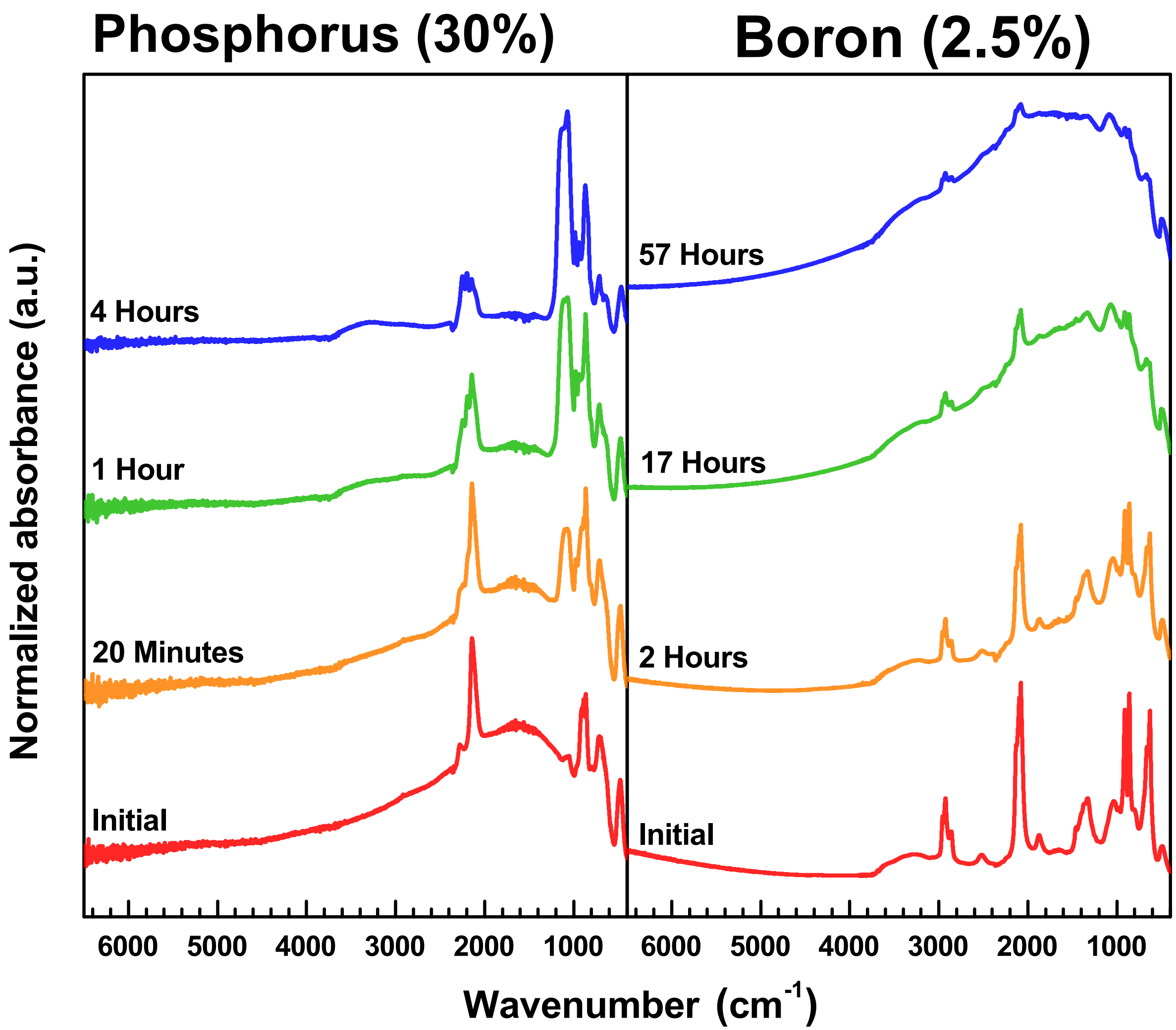




LSPR observation indicates some P in the NC core… but where's the rest?

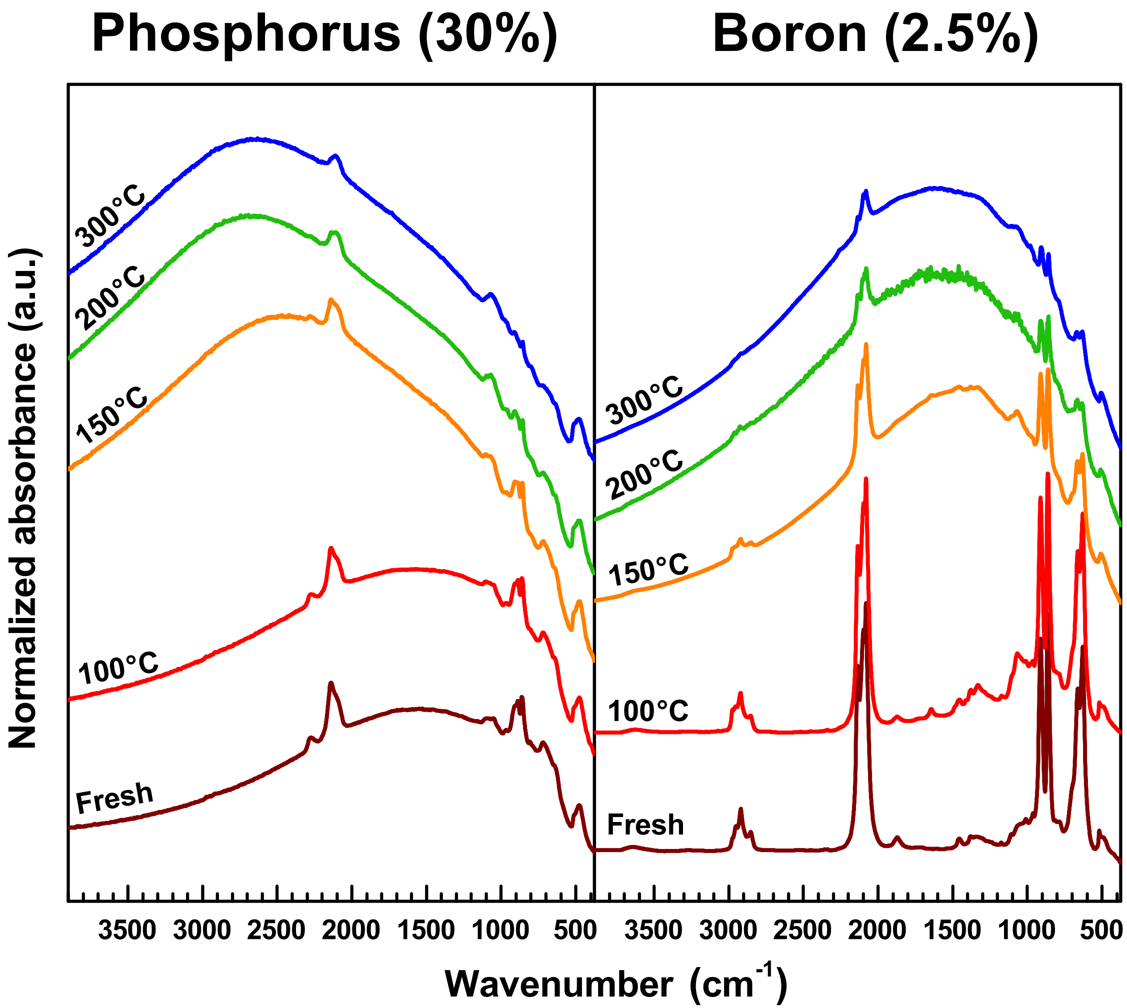
D. J. Rowe, J. S. Jeong, K. A. Mkhoyan, and U. R. Kortshagen, Nano Letters **13**, 1317 (2013)

Influence of surface: oxidization



Kramer, N. J.; Schramke, K. S.; Kortshagen, U. R. *Nano Letters*, **15 (8)**, 5597-5603, (2015)

Plasmonic response of doped NCs

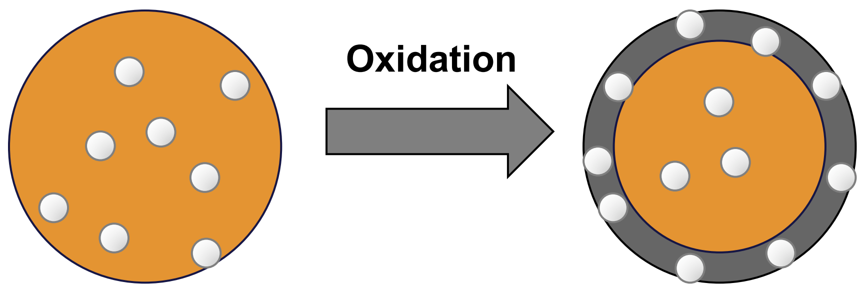


D. J. Rowe, J. S. Jeong, K. A. Mkhoyan, and U. R. Kortshagen, Nano Letters **13**, 1317 (2013)

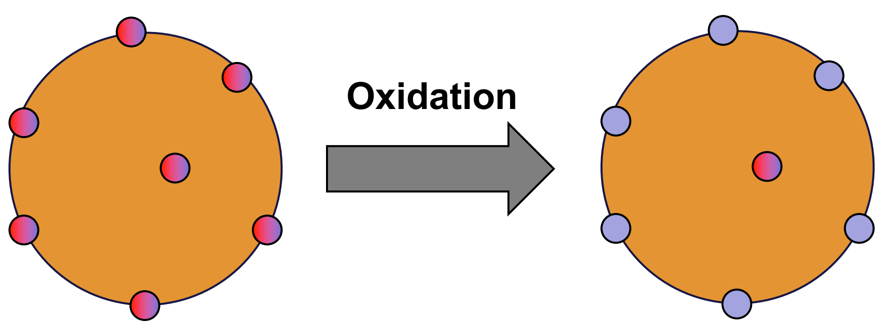
Kramer, N. J.; Schramke, K. S.; Kortshagen, U. R. *Nano Letters*, **15 (8)**, 5597-5603, (2015)

Role of surface in Si NC plasmonics

- P-doped Si NCs: substitutional P doping with trap generation at Si/SiO_x interface



- B-doped Si NCs: in addition to substitutional B, likely surface doping potentially through BO_x groups



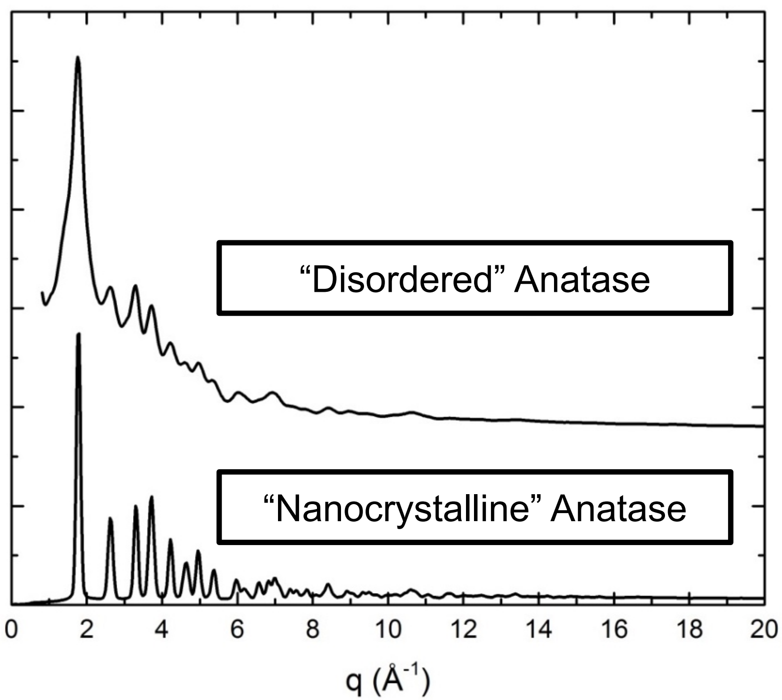
BO_x acceptors?

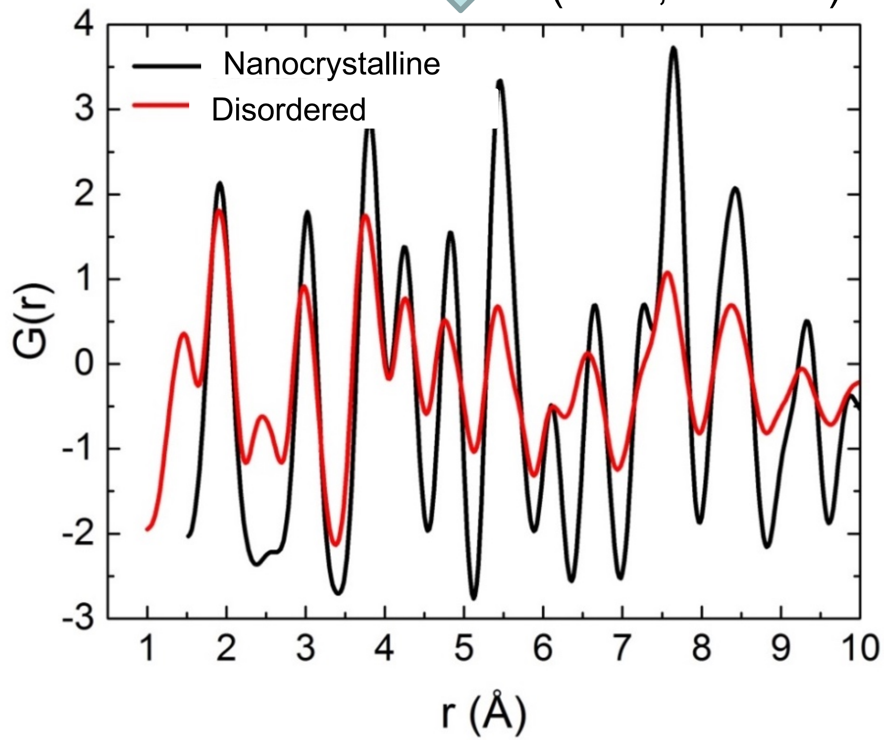
Pair distribution function analysis

- Atomic pair distribution function (PDF) analysis → Fourier transform of high energy XRD pattern into atomic pair distances

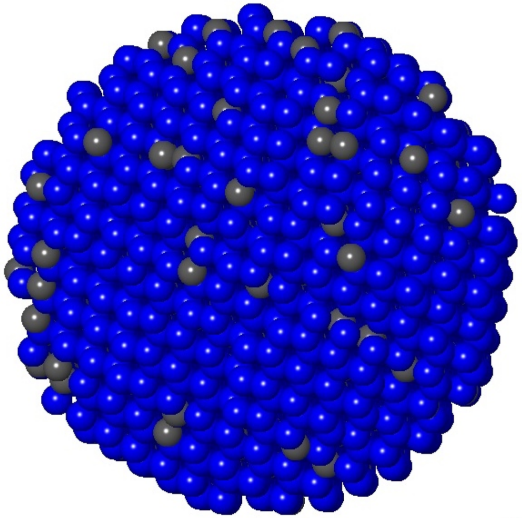
$$G(r) = (2/\pi) \int_{Q=0}^{Q_{max}} Q[S(Q) - 1] \sin(Qr)\, dQ$$

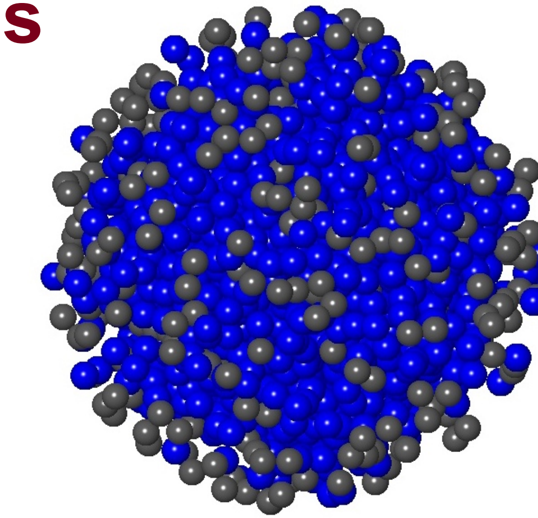
Nick Bedford (NIST, Boulder)

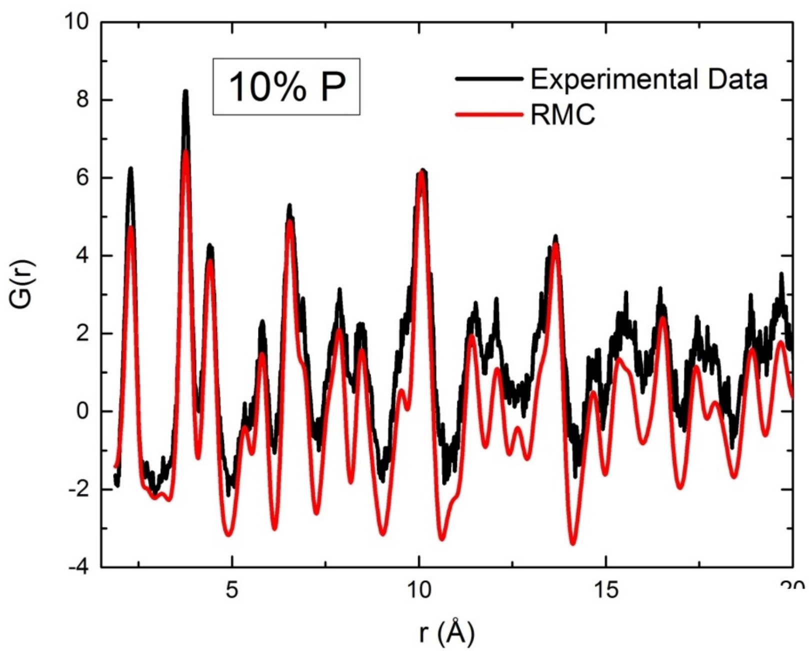




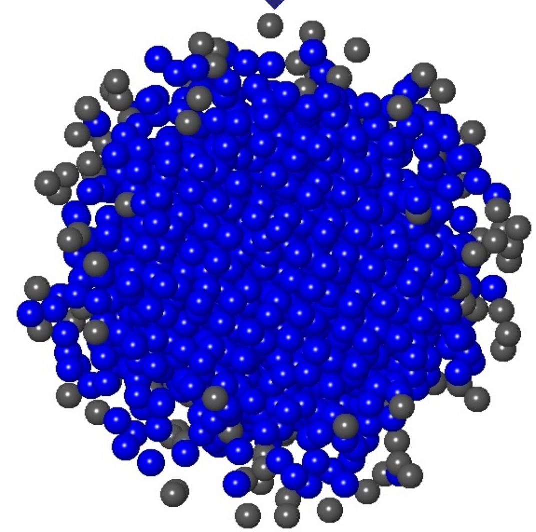
RMC of doped Si NCs



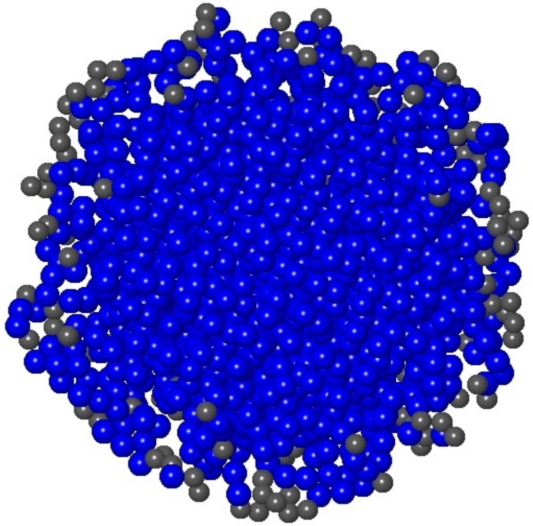


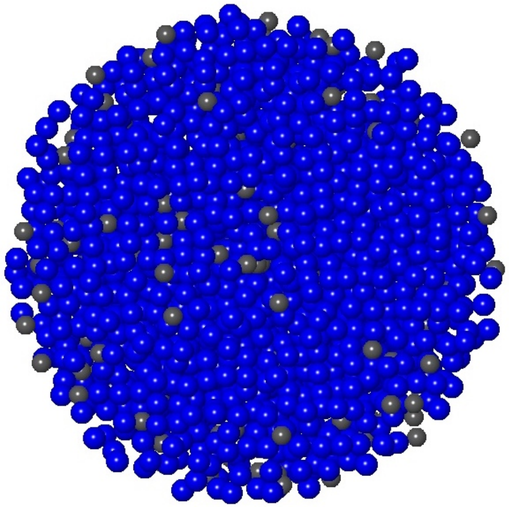


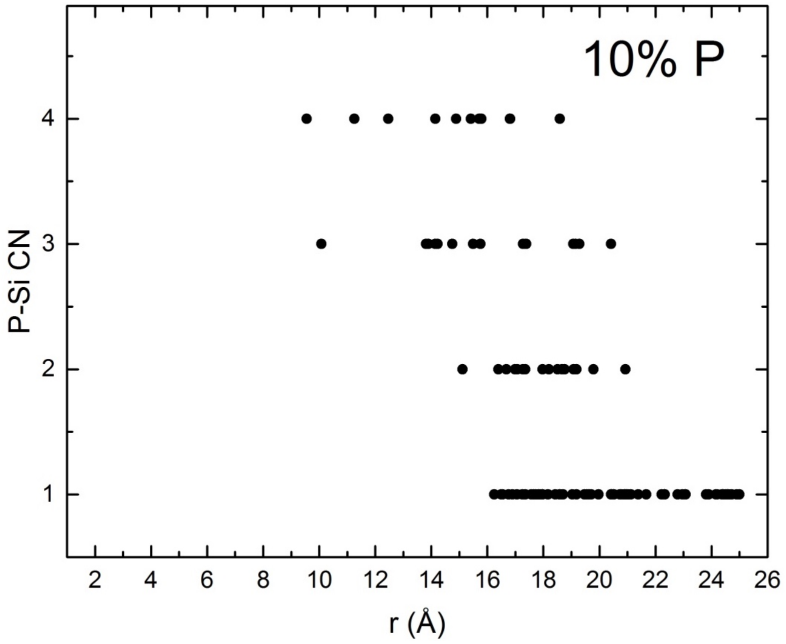
cross section

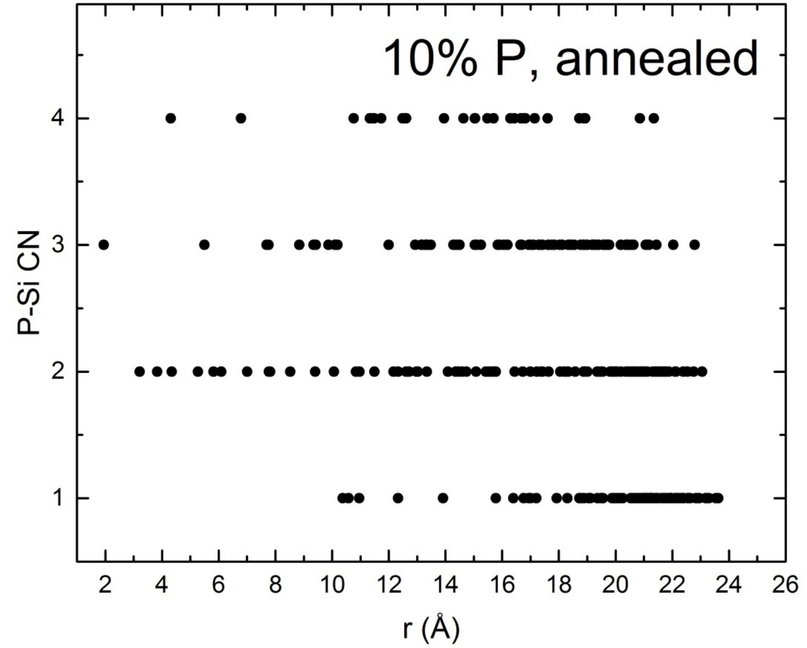


10% P-doped Si NCs





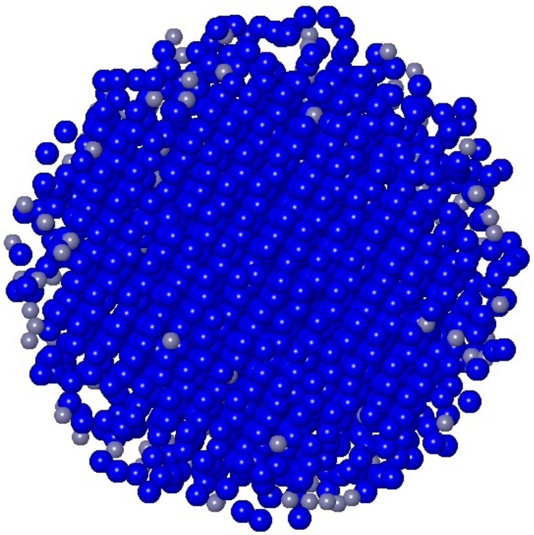


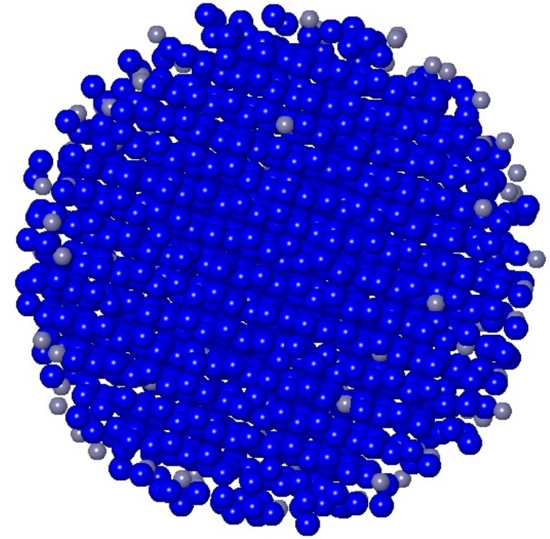


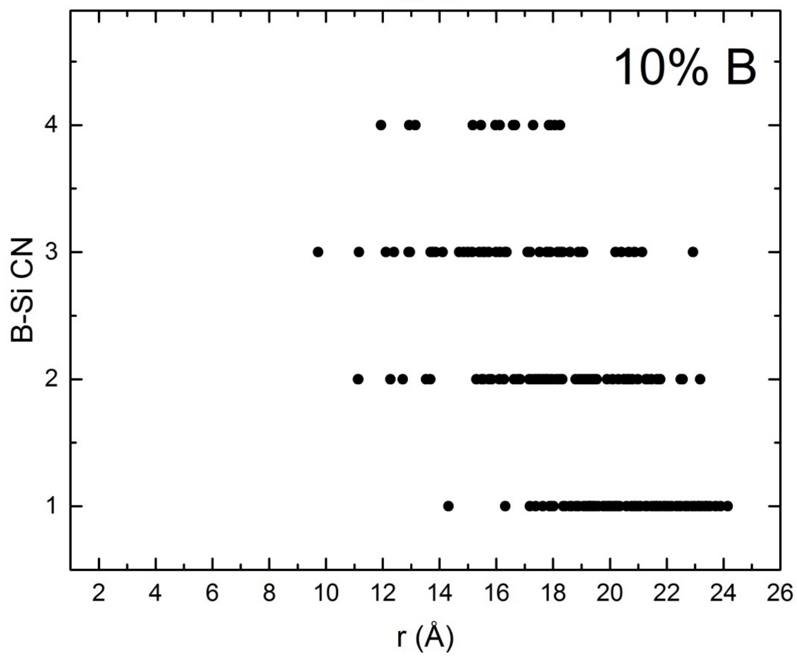
as deposited

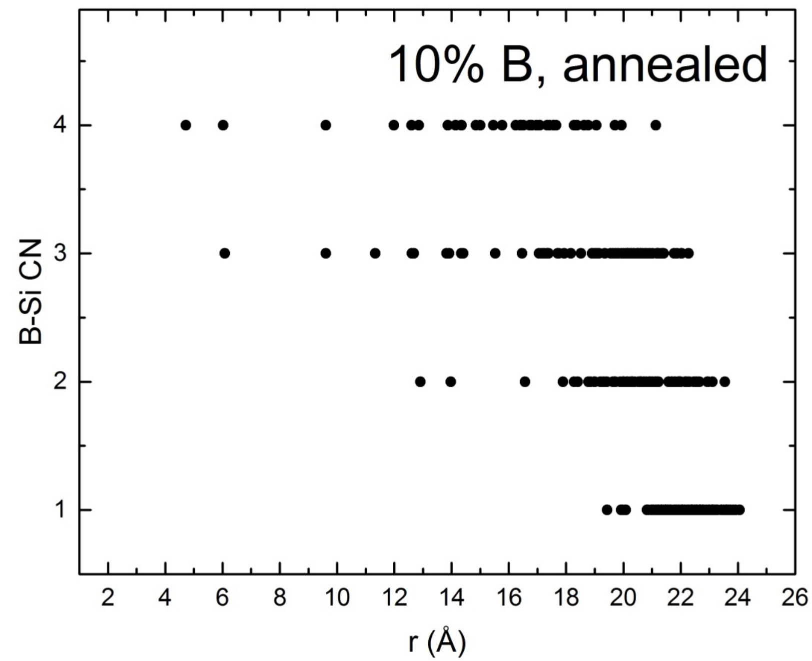
annealed at 200 ºC, 30 min

10% B-doped Si NCs









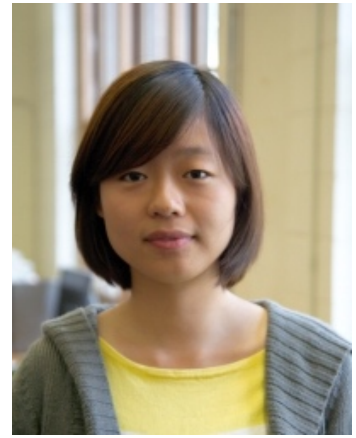
as deposited

annealed at 200 ºC, 30 min

Ting Chen

Nic Kramer

Konstantin Reich

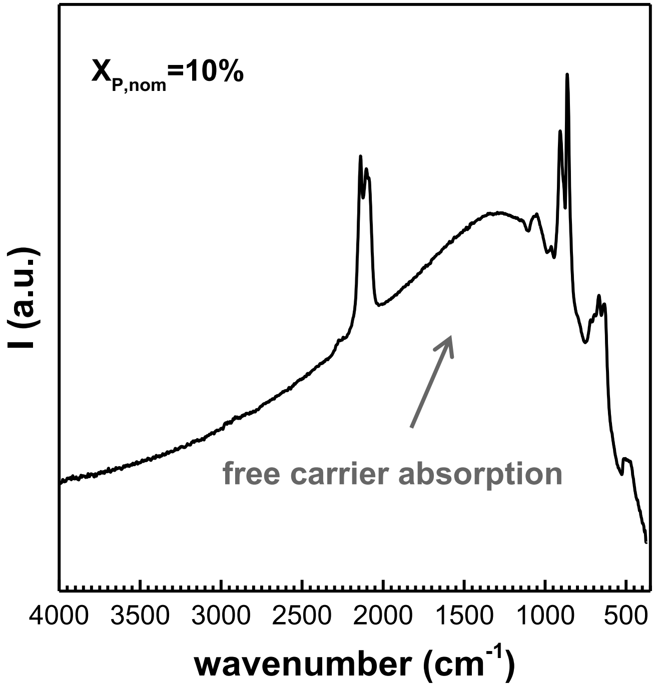


Han Fu

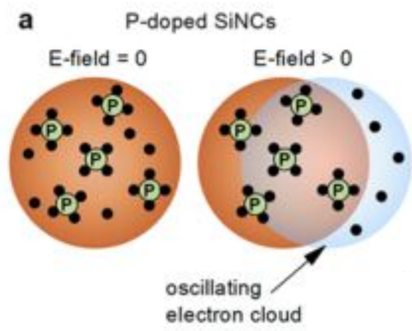
Boris Shklovskii

Electronic transport in nanocrystal films

Free electrons in P-doped Si NCs



Localized surface plasmon resonance (LSPR)

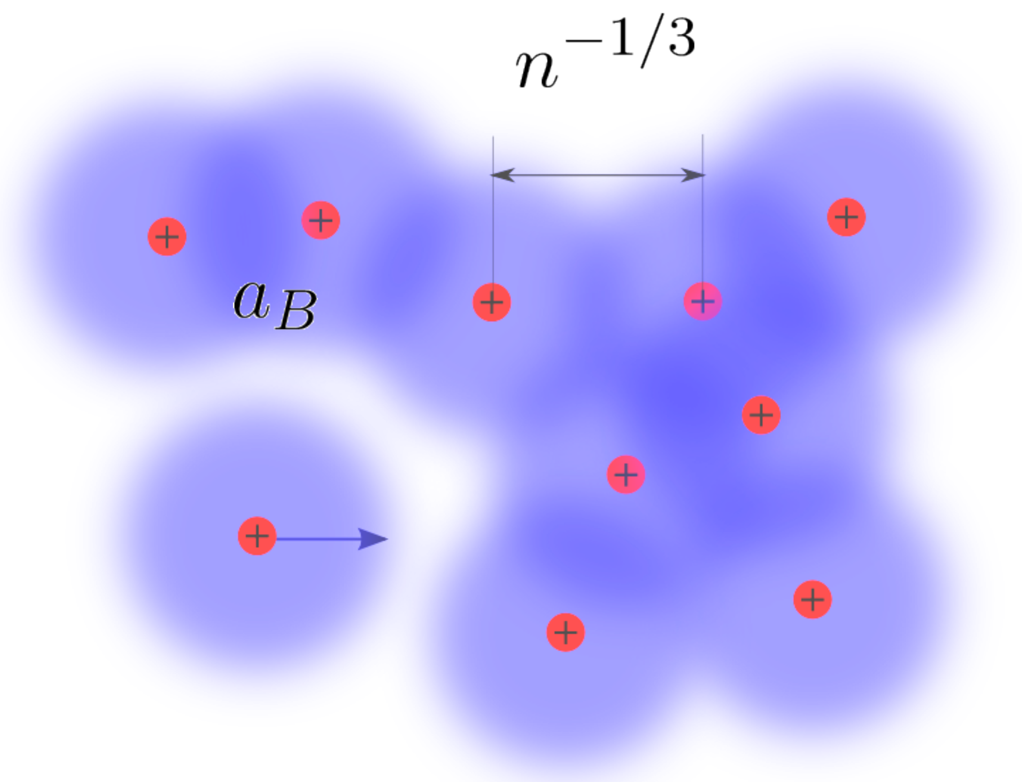


$$f_{LSPR} = \frac{1}{2\pi}\sqrt{\frac{n_{fc}e^2}{\varepsilon_0 m_e^*(\varepsilon_{Si} + 2\varepsilon_m)}}$$

$$n_{fc} > 2.2\times10^{19}\ \text{cm}^{-3}$$

$X_{P,\,nom}$ (%)	d (nm)	n (10^{20} cm^{-3})	N_P	$N_{P,\,active}$	$N_{P,\,active}/N_P$ (%)
1	8.1	-	65	-	-
2	8.0	-	110	-	-
3	8.0	-	210	-	-
5	8.0	1.9	320	51	16
10	7.5	2.4	442	53	12
20	7.1	2.8	644	52	8

Metal to insulator transition in bulk semiconductors



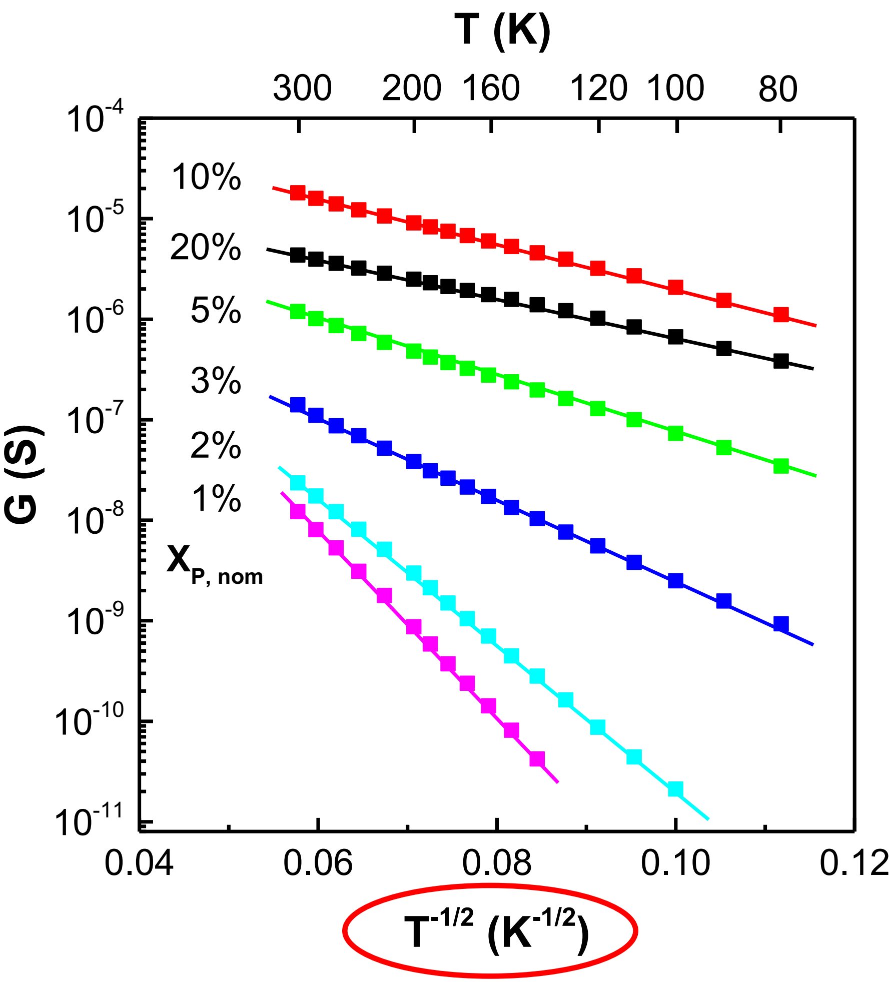
Metal-Insulator Transition in bulk semiconductors

Mott criterion: $n_M a_B^3 \approx 0.02$

Si: $n_M \approx 3 \times 10^{18}$ cm^{-3}

CdSe: $n_M \approx 2 \times 10^{17}$ cm^{-3}

How far do electrons hop?



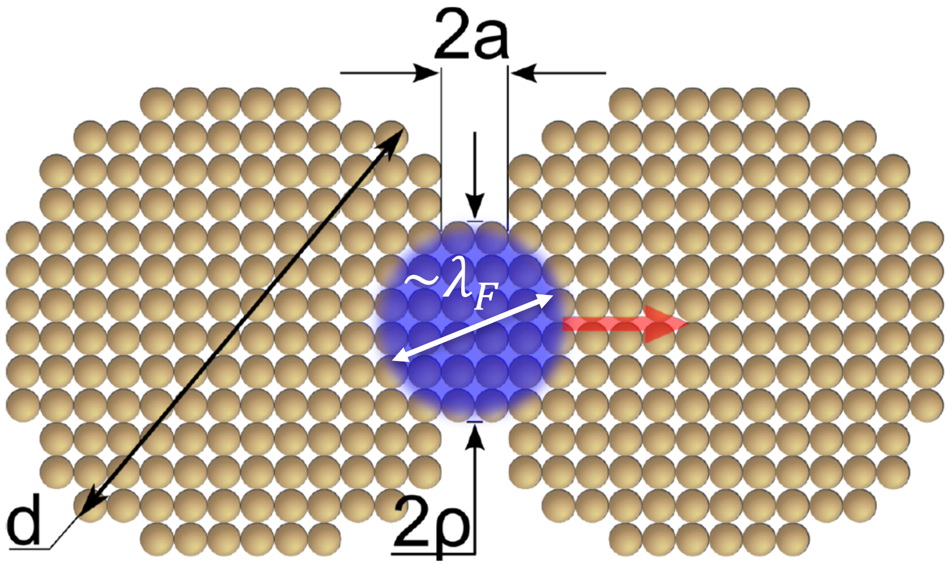
Characteristic temperature:

$$T_{\mathrm{ES}} = \frac{2.8e^2}{4\pi k_{\mathrm{B}} \varepsilon \xi}$$

Localization Length

T. Chen, K. Reich, H. Fu, N. Kramer, U. Kortshagen, B. Shklovskii,, *Nat. Mater.* **15**, 299 (2016)

Theory of metal-insulator transition in NC films



$k_F\rho \approx 2$ or $\lambda_F \approx \rho/2$

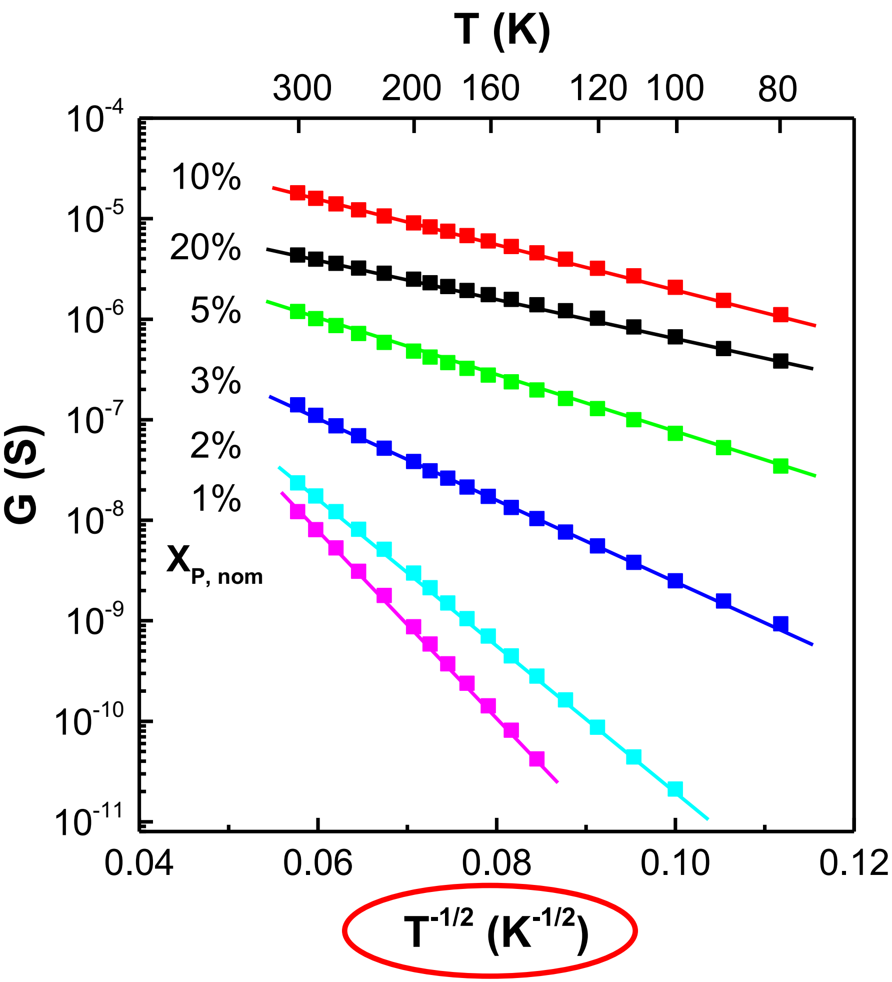
$n_c\rho^3 \approx 0.3g$

$$k_F = \left(\frac{3\pi^2}{g}n\right)^{1/3} \qquad \lambda_F = \left(\frac{g}{3\pi^2 n}\right)^{1/3}$$

material	g	n_c (cm^{-3})	n_{mott} (cm^{-3})
Si	6	5×10^{20}	3×10^{18}
CdSe	1	2×10^{20}	2×10^{17}

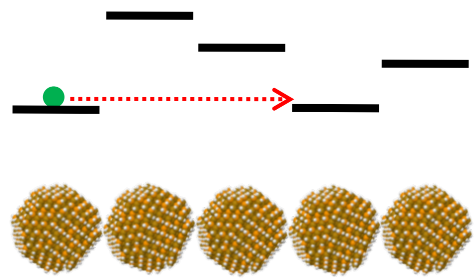
T. Chen, K. Reich, H. Fu, N. Kramer, U. Kortshagen, B. Shklovskii,, *Nat. Mater.* **15**, 299 (2016)

T-dependent conductance in P-doped Si



Efros-Shklovskii variable range hopping

(A L Efros and B I Shklovskii , J. Phys. C8, L49 (1975))



NCs are randomly charged

$$G \propto \exp\left[-\left(\frac{T_{ES}}{T}\right)^{1/2}\right]$$

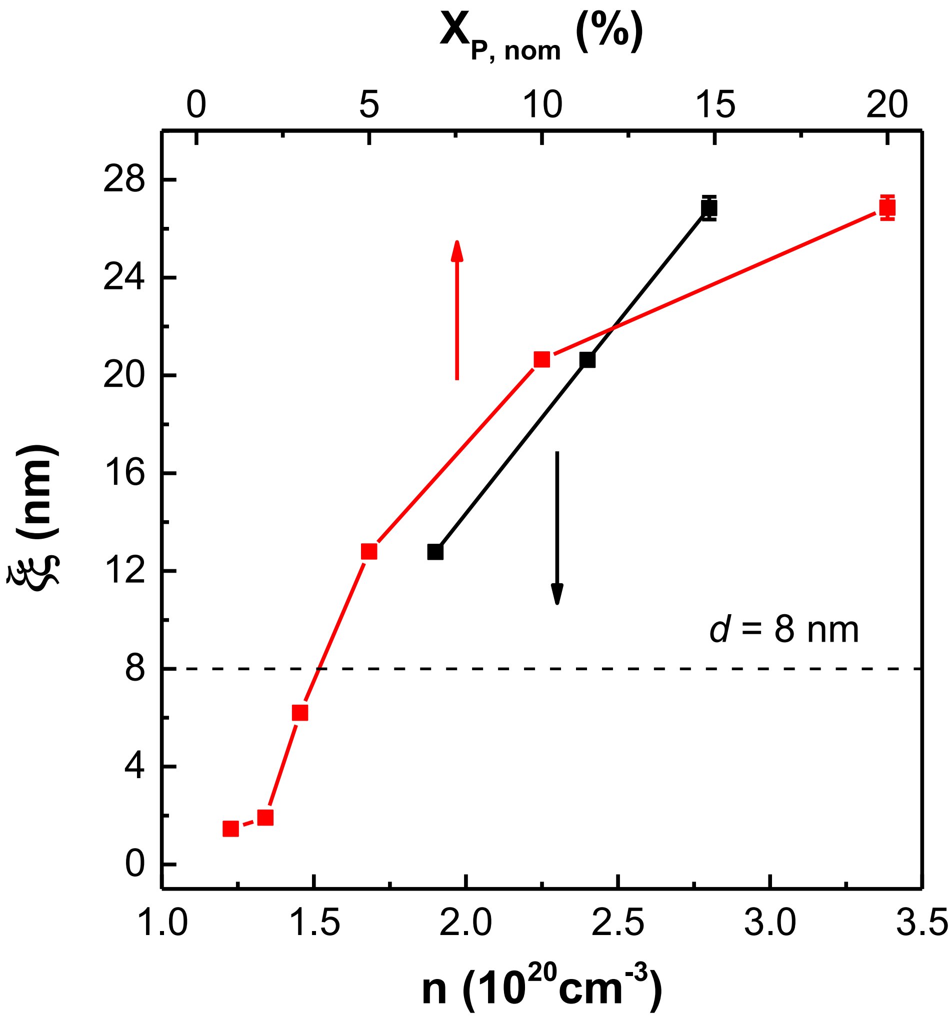
characteristic temperature:

$$T_{ES} = \frac{2.8e^2}{4\pi k_b \varepsilon \xi}$$

localization length

T. Chen, K. Reich, H. Fu, N. Kramer, U. Kortshagen, B. Shklovskii, *Nat. Mater.* **15**, 299 (2016)

Approaching the metal-insulator transition



T. Chen, K. Reich, H. Fu, N. Kramer, U. Kortshagen, B. Shklovskii,, *Nat. Mater.* **15**, 299 (2016)


Ben Greenberg


Zach Robinson


Claudia Gorynski


Bryan Voigt

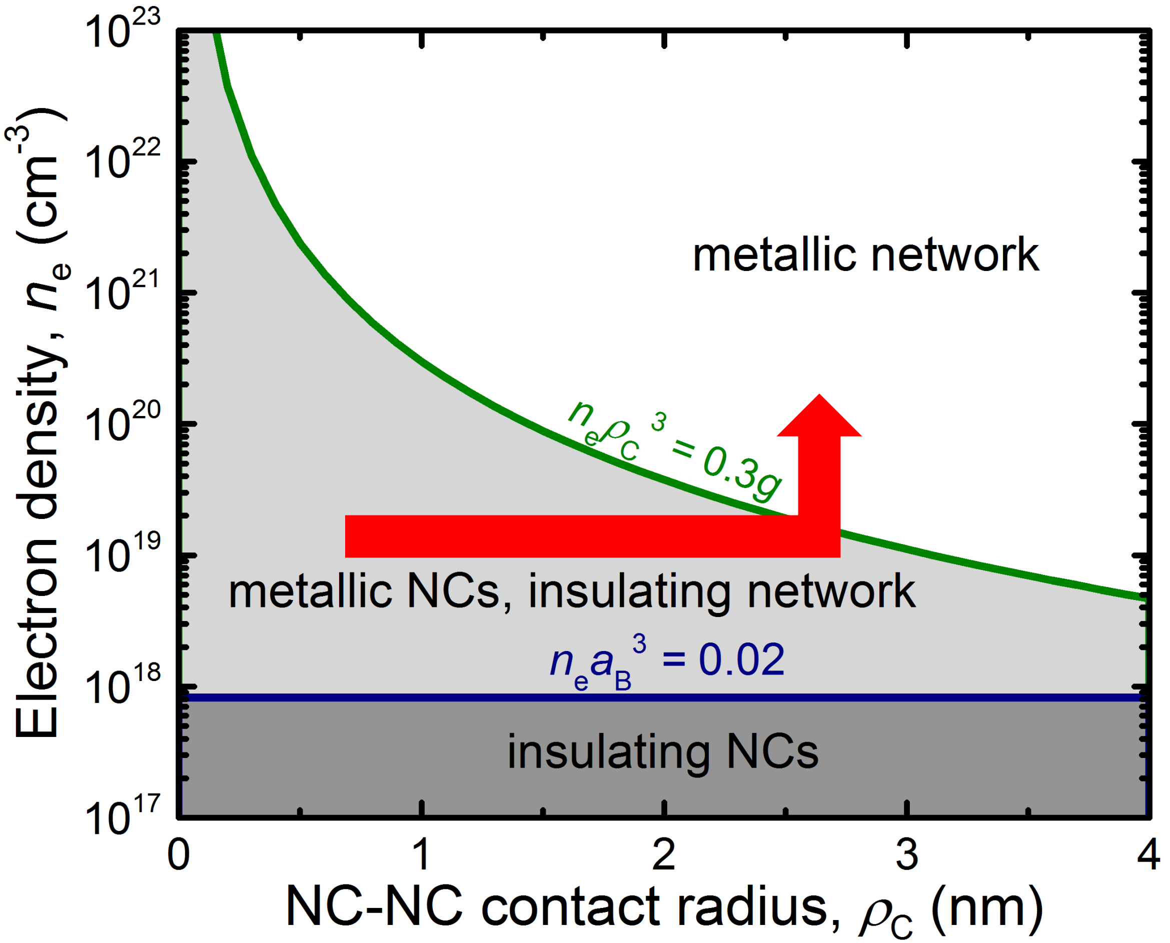

Lorraine Francis


Eray Aydil

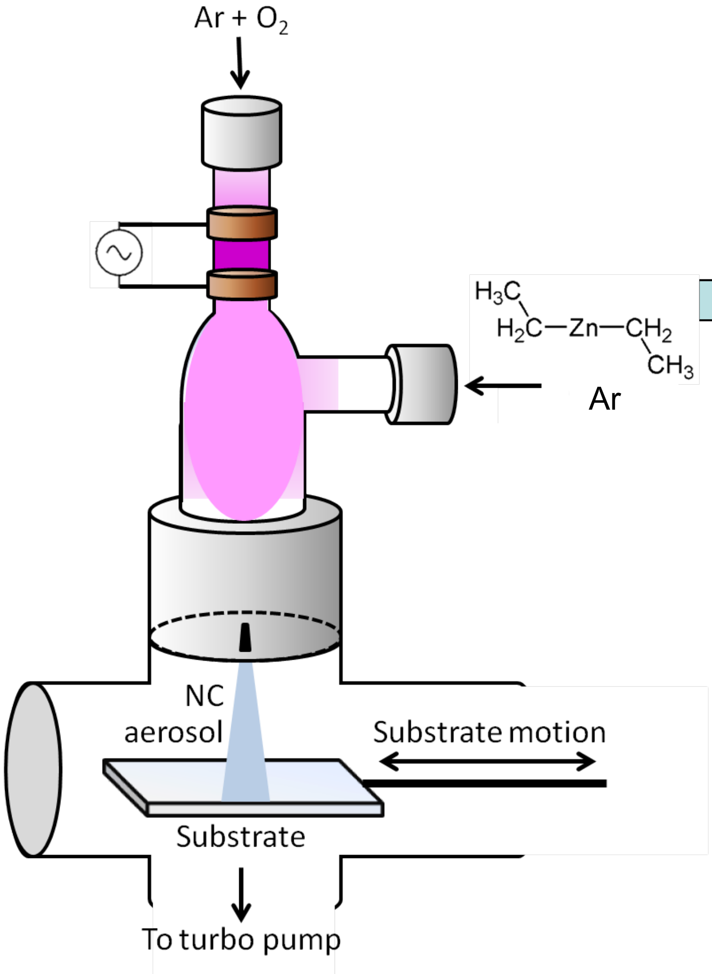
Crossing IMT in ZnO NC films?

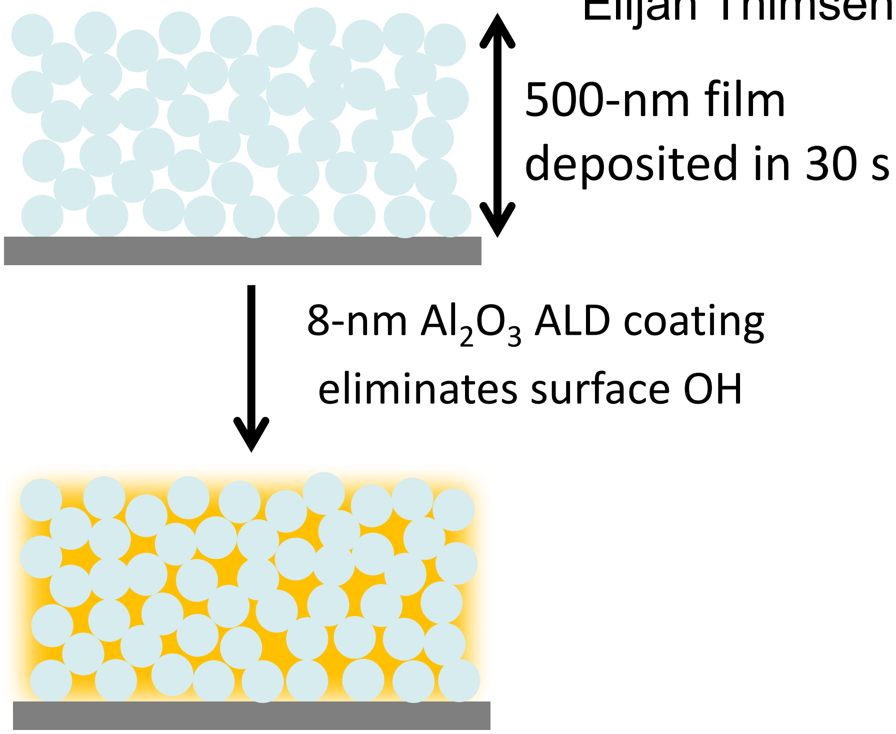
(submitted)

Importance of contact for metal-insulator transition



Plasma synthesis of ZnO NCs





Thimsen, E., M. Johnson, X. Zhang, A.J. Wagner, K.A. Mkhoyan, U.R. Kortshagen, and E.S. Aydil, Nature Communications **5**, 5822 (2014)

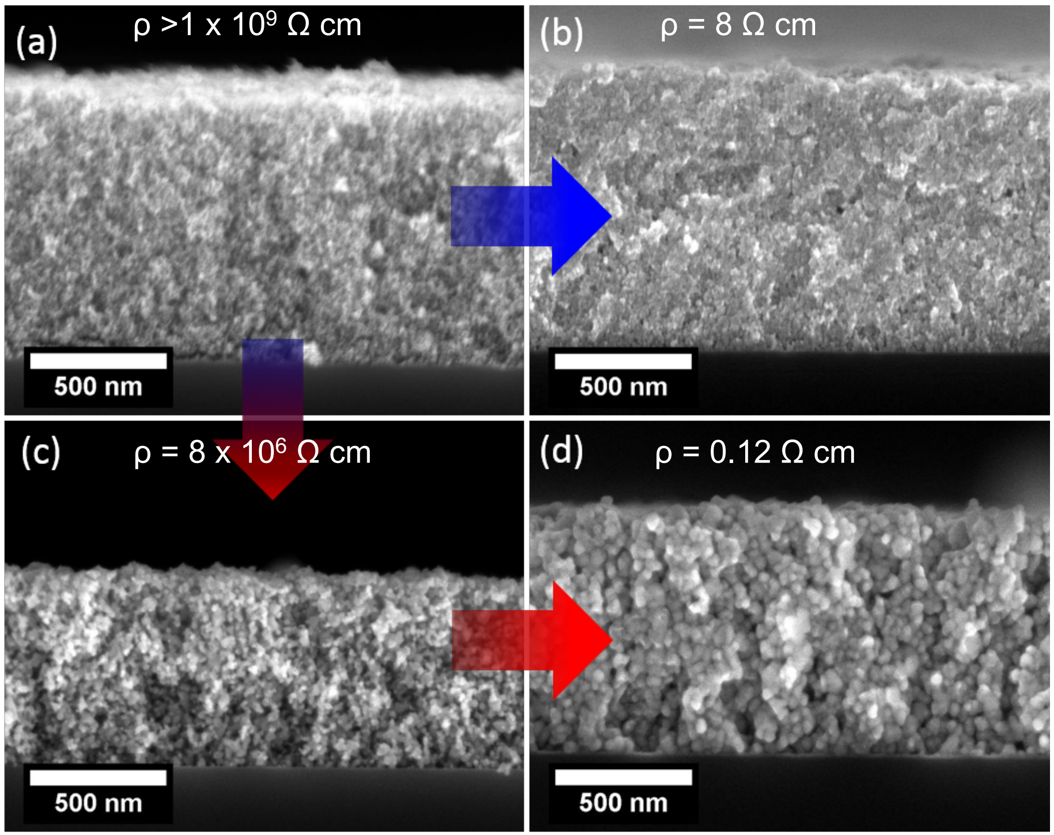
Electrical properties

After coating with ALD Al_2O_3

No ALD coating

As-deposited ZnO NC film

Annealed ZnO NC film

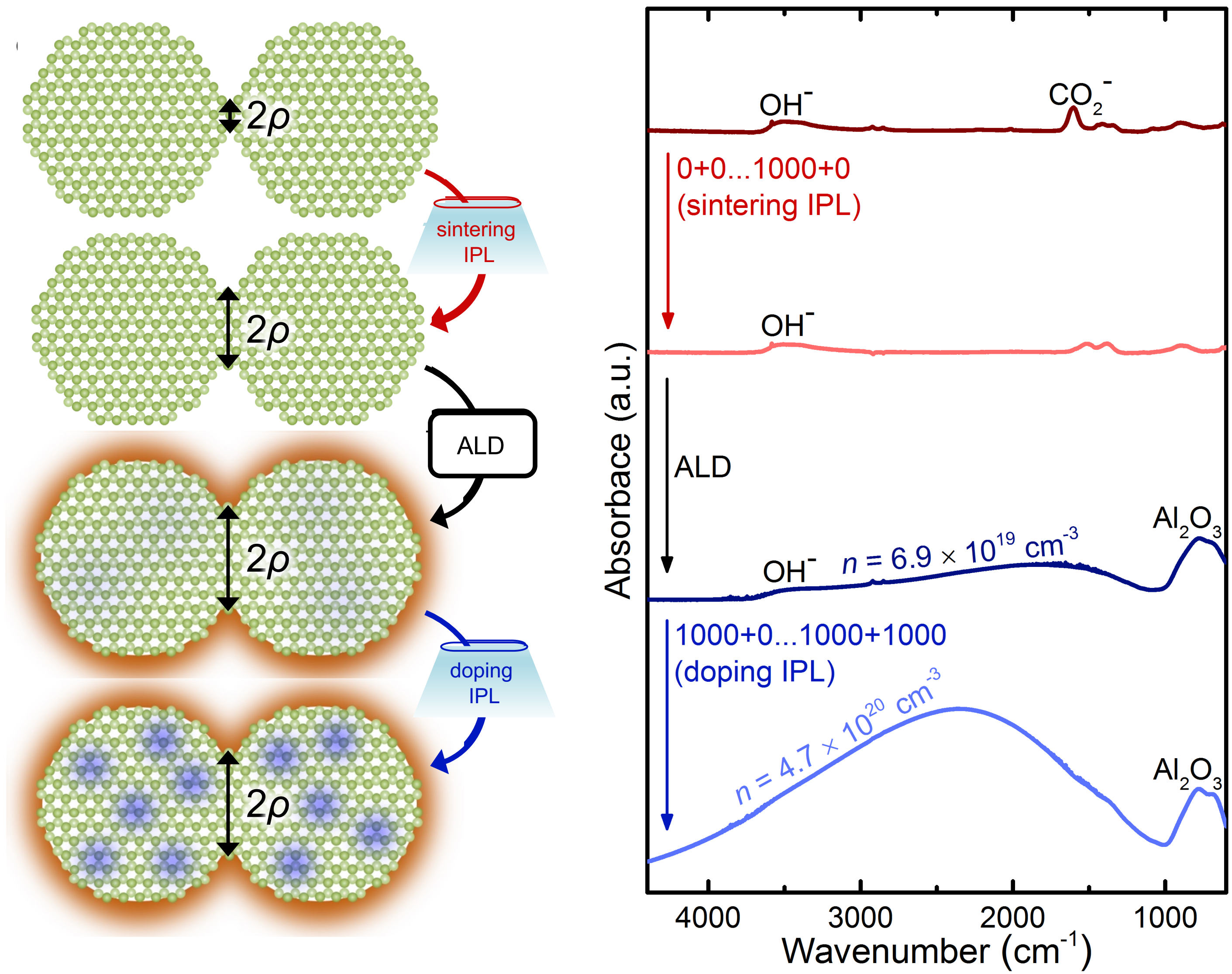


μ_e=0.1 cm^2/Vs

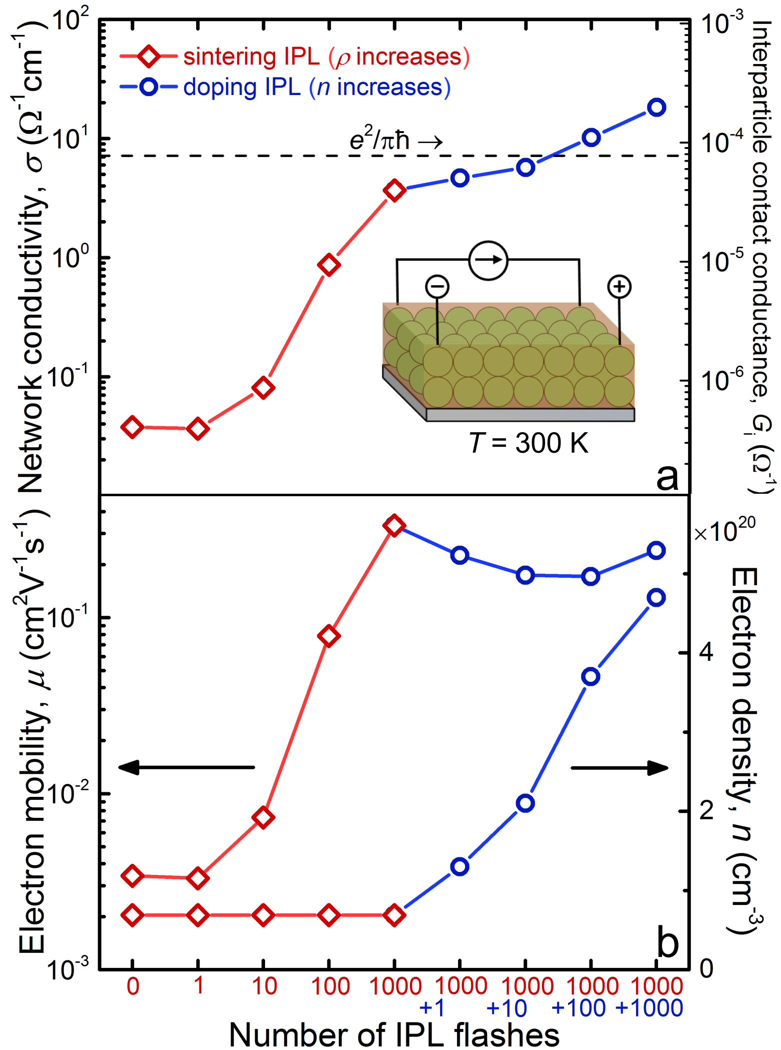
μ_e=3.0 cm^2/Vs

Thimsen, E., M. Johnson, X. Zhang, A.J. Wagner, K.A. Mkhoyan, U.R. Kortshagen, and E.S. Aydil, Nature Communications **5**, 5822 (2014)

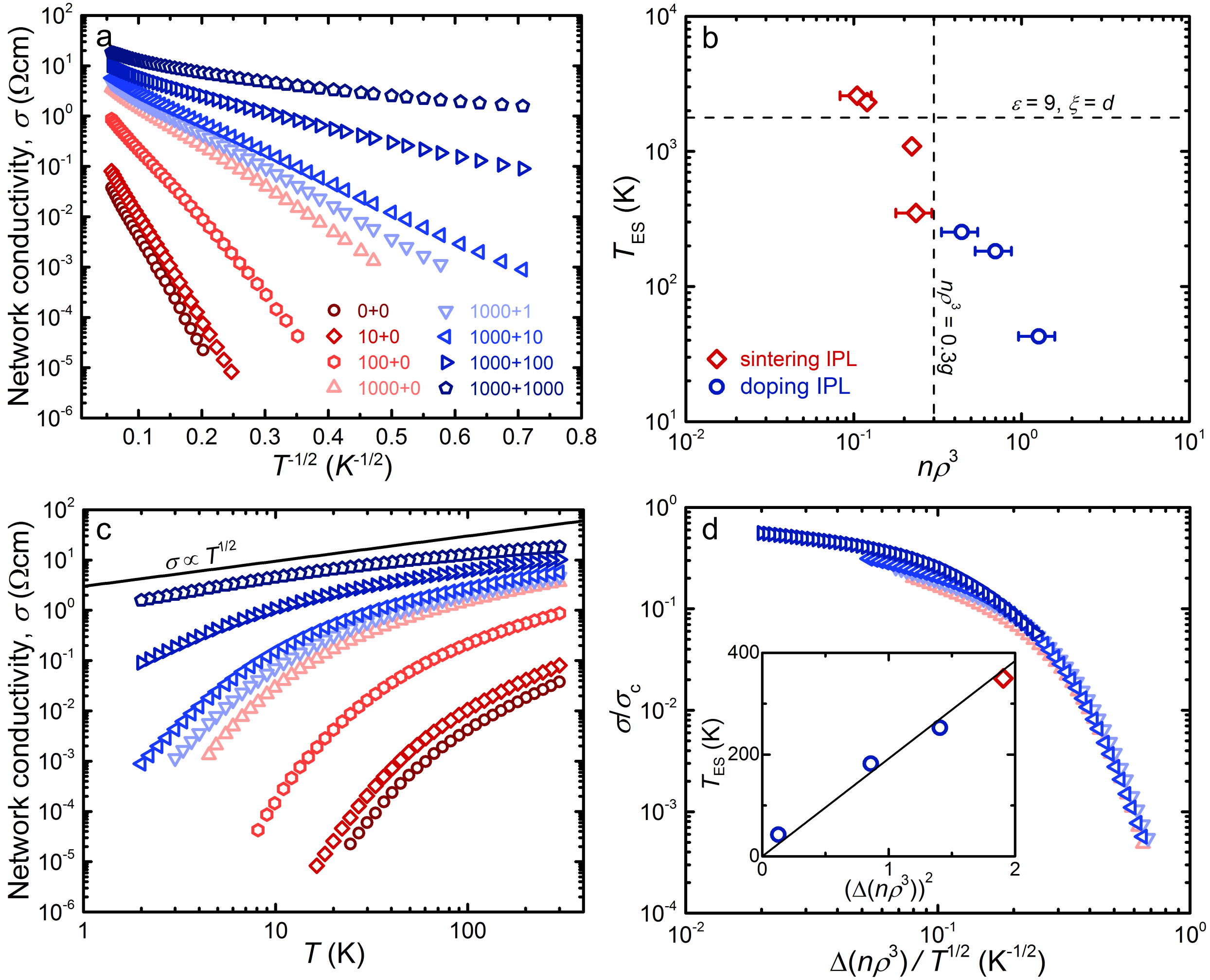
Intense Pulsed Light sintering to tune mobility and carrier density



Tuning mobility and carrier density



Approaching the insulator-metal transition



Summary

- Plasma Synthesis of nanocrystals suitable for high-melting point materials
- Plasmonic response of highly P- and B-doped Si QDs
- Theory of metal-insulator transition in doped nanocrystal films supported by measurements in P-doped Si NCs and recent measurements in ZnO NC films

Acknowledgments

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